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Occurrence and levels of selected compounds in European Sewage Sludge Samples

Results of a Pan-European Screening Exercise (FATE SEES)

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Abstract

This report describes the work conducted by the European Commission's Joint Research Centre in the context of an Administrative Arrangement between DG Environment and the JRC. The work aimed at technical support in the establishment of an approach to identify and prioritise among relevant compounds that have to be considered in European regulation dealing with Sewage Sludge. Particular emphasis was given with regard to resilience in soil or the ability to compromise ecosystems adjacent to sludge-receiving soils.

The work includes the results of a targeted and independent screening of typical European situations of sewage sludges with regard to the occurrence and levels of compounds of concern, many of which never assessed in a pan-European dimension.

In total, 63 samples, mostly taken as grab samples and originating from 15 countries, were assessed for 22 minor and trace elements and 92 organic compounds including ingredients of personal care products and pharmaceuticals. The underlying analytical methods are carefully documented with regards to their performance characteristics. Obtained results are assessed statistically and where possible compared to other findings. Although the analysed single samples are insufficient to make any statement on the performance of the treatment processes leading to the sewage sludge, the collective of data allows having a glance at the pan-European situation as regards the studies compounds.

Background information from literature describing the situation before the survey is included. To assess the availability of selected persistent organic pollutants, findings of long-term case study are included, too.

Participating laboratories and roles

The findings presented in this report are the result of a large collaborative effort. For confidentiality reasons, the identities of the participating Waste Water Treatment Plants cannot be revealed in this public report, but are known to the European Commission. This anonymity shall not minder our acknowledgment of the considerable support and in-kind contribution behind the exercise.

As regards the practical execution of the project organization and the work in the laboratories the following persons contributed actively.

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- Michela Ghiani (Technical correspondence and liaison with sites)
- Sara Comero (ICP-AES, CV-AAS, Statistical evaluation)
- Robert Loos (Perfluoroalkyl substances; PFAS)
- Simona Tavazzi, Bruno Paracchini (LC-MS/MS)
- Gert Suurkuusk, Giulio Mariani (GC-MS)
- Gunther Umlauf (long-term study on POPs)
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- Werner Hartl (GC-MS)

List of Abbreviations and Symbols

Throughout this report the following abbreviations and symbols[1] are used:

2,4-D	2,4-Dichlorophenoxyacetic acid
2,4,5-T	2,4,5-Trichlorophenoxyacetic acid
AAS	atomic absorption spectrometry
AES	atomic emission spectrometry
AMA	advanced mercury analyzer
BCR	Bureau Communautaire de Reference
BDL	below detection limit
CRM	certified reference material
CV	cold-vapour
CV%	coefficient of variation
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
D6 = Dodecamethylcyclohexasiloxane	
DEA	diethyl-ammonium
DDC	diethyl-dithiocarbamate
DG	Directorate-General
DL	dioxin-like
EC	European Commission
EU	European Union
F	factor (from PMF)
EVF	explained variation of factor
GC	gas chromatography
ICP	inductively coupled plasma
IES	Institute for Environment and Sustainability
IUPAC	International Union for Pure and Applied Chemistry
JRC	Joint Research Centre
k	coverage factor
K_{OW}	octanol/water partition coefficient
LC	liquid chromatography
LoD	limit of detection
LoQ	limit of quantification
MCPA	2-methyl-4-chlorophenoxyacetic acid
MDL	method detection limit
MDM	Octamethyltrisiloxane
MD2M	Decamethyltetrasiloxane
MD3M	Dodecamethylpentasiloxane
MRM	multiple reaction monitoring
MS	mass spectrometry
PAH	polyaromatic hydrocarbon
PCA	principal component analysis
PCB	polychlorinated biphenyls
PCM	polycyclic musk
PFASs	perfluoroalkyl substances
PCDD/F	polychlorinated dibenzo-dioxin/furane
PFNA	perfluorononanoic acid
PFOA	perfluorooctanoic acid
PFOS	perfluorooctane sulfonate
PMF	positive matrix factorization
POP	persistent organic pollutant
r	repeatability
SOP	standard operation procedure
SRM	standard reference material
SSL	sewage sludge
STD	standard deviation
STP	sludge treatment plant
$u_{combined}$	combined uncertainty
U	expanded uncertainty
$u_{(r)}$	combined uncertainty for repeatability
$u_{(IP)}$	combined uncertainty for repeatability
$u_{(t)}$	combined uncertainty for repeatability
UHPLC	Ultra High Pressure Liquid Chromatography
U.o.M.	unit of measurand
US	United States of America
WGS84	World Geodetic System 1984
WWTP	waste water treatment plant

[1] Chemical elements are identified by the respective symbol according IUPAC

Table of Contents

List of Tables

List of Figures

1 Introduction

Directive 86/278/EEC [**1**], the so-called Sewage Sludge Directive, was adopted with a view to encourage the application of sewage sludge in agriculture and to regulate its use in such a way as to prevent harmful effects on soil, vegetation, animals and man. The use of sewage sludge must not impair the quality of the soil and of agricultural products. Sewage sludge contains nutrients and organic matter, but it contains also contaminants such as heavy metals, persistent organic pollutants and pathogens.

The present directive sets limit values for only 7 heavy metals: cadmium, copper, nickel, lead, zinc, mercury and chromium in soil as well as in sludge itself. It does not consider persistent organic pollutants (POPs) such as dioxins, polyaromatic hydrocarbons, nor potentially pathogenic organisms, or newer, less investigated compounds spread deliberately or accidentally into the environment. Some substances and substance classes, like for instance endocrine disruptors or engineered nanomaterials, may pose potential risks that science is only starting to understand.

After 20 years since its adoption, the Directive appears to be entirely outdated. Indeed, Member States have – on the basis of new scientific insight in the effects of sludge on land – enacted and implemented much stricter limit values for heavy metals as well as for contaminants, which are not addressed in the Directive.

A study executed for DG Environment on environmental, economic and social impacts from the revision of the Sewage Sludge Directive concluded that no measureable risk has been identified from the organic compounds in sewage sludge [**2**]. However, the same study stated the lack of data known in quality and of good comparability for many organic substances. In order to verify current level of presence of organic contaminants in sewage sludge it was deemed necessary to conduct a targeted monitoring exercise following a similar approach in the US [**3**]. As being expressed by a Communication of the Commission on future steps in bio-waste management [**4**], a potential extension of the scope the revision of the Sewage Sludge Directive was at the basis of the monitoring design. In order to address this question whether the revised Directive could cover other biodegradable waste, it was deemed valuable that biowastes would be subject to a similar test exercise.

The 2006 incident with perfluorinated surfactants in North-Rhine Westphalia, Germany, although not related an appropriate use of sewage sludge, jeopardized at the end the drinking water quality in the affected area and led to the need to intensify exploratory monitoring on what is commonly called emerging or less-investigated pollutants. It is however, worth to mention that this example of contamination turned out to originate from local fields treated with a fertilizer containing a mixture of food/industry sewage sludges. The incident once more underlined the need to finally address the issue of organic contaminants in sewage sludge.

Within this setting, the European Commission's in-house science service, the Joint Research Centre, was asked to establish an independent screening and snapshot of the current situation regarding the occurrence and levels of problematic compounds, many of which never been assessed in a pan-European dimension. The exercise was conducted within the so-called FATE Project[2] as FATE-SEES on **s**ewage sludges and **e**ffluents for **e**merging **s**ubstances.

The findings of the FATE-SEES survey together with some further background information as well as the results of a long-term case study investigating the long-term accumulation of some selected persistent organic pollutants (POPs) are presented in the following.

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[2] *The FATE Programme aims at the study of the fate of environmental pollutants in aquatic and terrestrial ecosystems*

The pan-European snapshot evaluated the concentration of 114 analytes, including minor and trace elements, aromatic hydrocarbons (PAHs), perfluoroalkyl substances (PFAs), pesticides, benzotriazoles, personal care products, sweeteners and pharmaceuticals.

Table 1 Chemicals analyzed in the FATE-SEES survey

Class	*Compound*	***Class***	*Compound*
Minor and Trace elements	Ag	**Phenols**	Nitrophenol
	Al		2,4-Dinitrophenol
	As	**Sweeteners**	Acesulfame K
	Ba		Sucralose
	Cd		Saccharin
	Co	**Pharmaceuticals**	Acetylsalicylic acid
	Cr		Carbamazepine
	Cu		Ibuprofen
	Fe		Diclofenac
	Mg		Ketoprofen
	Mn		Naproxen
	Mo		Gemfibrozil
	Ni		Clofibric acid
	Pb		Bezafibrate
	Sb		Atenolol
	Se		Metopropol
	Ti		Propanolol
	V		Sotalol
	Zn		Tamoxifen
	P	**Pesticides**	Atrazine-desethyl
	K		Atrazine-desisopropyl
	Hg		Terbutylazine
PCM	Cashmerane		Terbutylazine-desethyl
	Celestolide		Terbutryn
	Phantolide		Simazine
	Traesolide		Propazine
	Galaxolide		Diuron
	Tonalide.		Isoproturon
PAH	Phenanthrene		Chlortoluron
	Anthracene		Linuron
	Fluoranthene		Alachlor
	Pyrene		Metolachlor
	Benzo(a)anthracene		Diazinon
	Chrysene		Molinate
	Benzo(b)fluoranthene		Metoxuron
	Benzo(k)fluoranthene		Hexazinone
	Benzo(e)pyrene		Carbaryl

Class	*Compound*	***Class***	*Compound*
	Benzo(a)pyrene		Carbendazim
	Perilene		Chloridazon
	Indeno(1,2,3-cd)pyrene		Chloridazon-desphenyl
	Dibenzo(a,h)anthracene		Chloridazon-methyl-desphenyl
	Benzo(g,h,i)perilene		Fenarimol
	Dibenzo(a,l)pyrene		Fenitrothion
	Dibenzo(a,h)pyrene		Flusilazole
	Dibenzo(a,i)pyrene		Iprodion
	Dibenzo(a,e)pyrene		Ioxynil
	Coronene		Imidacloprid
PFASs	PFOA		Methabenzthiazuron
	PFNA		Tolylfluanid
	PFOS		Vinclozolin
Personal care products	Triclosan		2,4-D
	Caffeine		2,4,5-T
	DEET		Mecoprop
Benzotriazoles	1H-Benzotriazole		Bentazone
	1-Methyl-benzotriazole		MCPA
	Benzothiazole		Dichlorprop
			Carbofuran

2 Status before the screening

2.1 Literature findings on organics in the period 2000-2009

Through the implementation of a number of Directives, Member States of the European Union must ensure that waste material is recorded, identified and managed in such a manner as to minimise the risk to human health and the state of the environment.
In addition to the Sewage Sludge Directive many Member States have on the bases of new scientific insight in the effects of sludge use on land enacted and implemented much stricter limit values for heavy metals as well as for contaminants which are not addressed in the Directive.
In this context, the knowledge about the occurrence and levels of organic chemicals appears to be crucial. Although in nearly all Member States sewage sludge to some major or lesser extent is used in agriculture, there is growing scepticism whether land application of sewage sludge is a sustainable method of dealing with that waste stream. The underlying concerns for these actions result in particular from the fact that the majority of contaminants in general and organic contaminants in particular potentially contained in sewage sludge are not known and not sufficiently tested before applying sludge on land. An extensive and meaningful risk assessment would require however full knowledge of the number, the concentration and the effects of all organic contaminants found in sewage sludge.
Filling the gaps in knowledge regarding the concentration, fate and toxicity of sludge-borne contaminants is critical if risks associated with land application are to be adequately characterized.
As a scene setter for FATE SEES, relevant literature on the occurrence of organic contaminants in European sludges basically during the last decade was reviewed. The situation before start of the monitoring appears as reported in the table below.

*Table 2 - Organic pollutants range concentration comparison reported in the literature including the EU Working Document on Sludge [**5**]*

Parameter/ Compound	Unit	Reported range of concentration	Range of concentration [µg/kg]	Reference Number
1. Aliphatics—short chained and chlorinated				
Butadiene, (hexachloro-1,3-)	ng/g	ND		[6]
Butane (1,2,3,4-diepoxy)	mg/m^3	ND		[7]
Methane	%	61-65		[8]
2. N-alkanes				
Polychlorinated n-alkanes	mg/kg d.w.	1.8-93.1	1800-93100	[9]
Propane (dichloro) isomers	mg/m^3	2.20	2200	[7]
3. Chlorobenzenes				
Benzene (hexachloro)	ng/g	6.80	6.80	[10]
4. Flame retardants				
Brominated diphenyl ether congeners (BDEs) total PBDEs	ng/g	0.3-11	0.3-11	[11]
Total PBDEs	ng/g	197-1185	197-1185	[12]
BDE 209	ng/g	81-1082	81-1082	[12]
BDE 209	µg/kg	138-617	138-617	[13]

Parameter/ Compound	Unit	Reported range of concentration	Range of concentration [µg/kg]	Reference Number
Penta-BDE	µg/kg	49-248	49-248	[13]
Tetrabromobisphenol A (TBBPA)	µg/kg	0.51	0.51	[14]
Hexabromocyclododecane (HBCD)	µg/kg	39-597	39-597	[13]
5. Organotins				
Butylitin (di)	mg/kg	0.264-8.557	264-85557	[15]
Butyltin (mono)	mg/kg	0.323-52.397	323-52397	[15]
Butyltin (tri)	mg/kg	0.264-43.564	264-43564	[15]
6. Perfluoroalkyl substances				
Perfluorooctane Sulfonate **(**PFOS)	ng/g	80-120	80-120	[16]
Perfluorooctane Sulfonate **(**PFOS)	ng/g	3-110	3-110	[17]
Perfluorooctanoate (PFOA)	ng/g	11.0-18	11.0-18	[16]
Perfluorooctanoate (PFOA)	ng/g	2-150	2-150	[17]
Fluorotelomer alcohols (FTOH)	ng/g	2-80	2-80	[17]
7. Personal care products and pharmaceuticals				
Acetaminophen	µg/l	29-246	29-246	[18]
Gemfibrozil	µg/l	0.07-0.40	0.07-0.40	[19]
Ibuprofen	µg/l	0.20-5.80	0.20-5.80	[20]
Ibuprofen	µg/l	34-168	34-168	[18]
Naproxen	µg/l	0.65-4.80	0.65-4.80	[20]
Salicylic acid	µg/l	<0.02-54	<0.02-54	[19]
Antibiotics				
Ciprofloxacin	ng/l	40-450	0.040-0.450	[21]
Ciprofloxacin	mg/kg	1.7-3.5	1700-3500	[22]
Doxycycline	mg/kg d.m.	1.3-1.5	1300-1500	[23]
Norfloxacin	ng/l	<24-180	<0.024-0.18	[21]
Norfloxacin	mg/kg	1.7-3.3	1700-3300	[22]
Ofloxacin	ng/l	<5.8-130	<0.0058-0.130	[21]
Triclosan (4-chloro-2-(2,4-dichlorophenoxy)-phenol and related compounds	µg/l	0.17-23.9	0.17-23.9	[24]
8. Fragrance material				
ADBI: 4-Acetyl-6-tert-butyl-1,1-dimethylindane (Celestolide),	µg/l or µg/kg d.m.	1.5-330	1.5-330	[25]
AMA: amino musk ambrette	µg/l or µg/kg d.m.	n.d.	n.d.	[25]
AMK: amino musk ketone,	µg/l or µg/kg d.m.	0.7-13.1	0.7-13.1	[25]
AMM: amino musk moskene	µg/l or µg/kg d.m.	0.1-36.2	0.1-36.2	[25]
AMT: amino musk tibetene	µg/l or µg/kg d.m.	n.d.	n.d.	[25]
AMX: amino musk xylene	µg/l or µg/kg d.m.	0.4-49.1	0.4-49.1	[25]
Cashmeran (DPMI) (6,7-dihydro-1,1,2,3,3-pentamethyl-4(5H)-indanone)	µg/l or µg/kg d.m.	1.7-93.3	1.7-93.3	[25]
Celestolide (1-[6-(1,1-Dimethylethyl)-2,3-dihydro-1,1-methyl-1H-inden-4-yl]-ethanone)	mg/kg d.m.	0.1-0.8	100-800	[26]

Parameter/ Compound	Unit	Reported range of concentration	Range of concentration [µg/kg]	Reference Number
Celestolide (1-[6-(1,1-Dimethylethyl)-2,3-dihydro-1,1-methyl-1H-inden-4-yl]-ethanone)	ng/l	1.4-1.5	0.0014-0.0015	[27]
Galaxolide (HHCB) (1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-benzopyran)	mg/kg d.m.	7.4-36.0	7400-36000	[26]
Galaxolide (HHCB) (1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-benzopyran)	µg/l	0.49-45.40	0.49-45.40	[20]
Galaxolide (HHCB) (1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-benzopyran)	ng/l	129.00-162.00	0.129-0.162	[27]
Galaxolide (HHCB) (1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-benzopyran)	ng/g	2709-3342	2709-3342	[28]
Galaxolide lactone (1,3,4,6,7,8-Hexahydro-4,6,6,7,8,8-hexamethylcyclopenta[g]-2-benzopyran-1-one)	mg/kg d.m.	0.8-3.5	800-3500	[26]
MA: 6-Methoxy-1-tert-butyl-2,4-dimethyl-3,5-dinitrobenzene (musk ambrette),	µg/l or µg/kg d.m.	n.d.	n.d.	[25]
MM: 1,1,3,3,5-Pentamethyl-4,6-dinitroindane (musk moskene)	µg/l or µg/kg d.m.	n.d.	n.d.	[25]
MT: 1-tert-Butyl-3,4,5-trimethyl-2,6-dinitrobenzene (musk tibetene),	µg/l or µg/kg d.m.	n.d.	n.d.	[25]
Musk Ketone (MK) (4-tertbutyl-3,5-dinitro-2,6-dimethylacetophenone)	µg/l or µg/kg d.m.	0.1-7.0	0.1-7.0	[25]
Musk Xylene (1-tert-butyl-3, 5-dimethyl-2,4,6-trinitrobenzene)	ng/l	12.00-16.00	0.012-0.016	[27]
Phantolide (1-[2,3-Dihydro-1,1,2,3,3,6-hexamethyl-1H-inden-5-yl]-ethanone)	mg/kg d.m.	0.2-1.8	22	[25]
Phantolide (1-[2,3-Dihydro-1,1,2,3,3,6-hexamethyl-1H-inden-5-yl]-ethanone)	ng/l	0.27-0.73	0.00027-0.00073	[27]
Tonalide (1-[5,6,7,8-Tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl]-ethanone)	ng/g	1343-1746	1343-1746	[29]
Tonalide (1-[5,6,7,8-Tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl]-ethanone)	ng/l	52.00-64.00	0.052-0.064	[27]
Tonalide (1-[5,6,7,8-Tetrahydro-3,5,5,6,8,8-hexamethyl-2-naphthalenyl]-ethanone)	mg/kg d.m.	3.4-11.2	3400-11200	[26]
Traseolide (ATII) (1-[2,3-Dihydro-1,1,2,6-tetramethyl-3-(1-methylethyl)-1H-inden-5-yl]ethanone	mg/kg d.m.	0.2-1.0	200-1000	[26]
Traseolide (ATII) (1-[2,3-Dihydro-1,1,2,6-tetramethyl-3-(1-methylethyl)-1H-inden-5-	ng/l	4.8-7.0	0.0048-0.007	[27]

Parameter/ Compound	Unit	Reported range of concentration	Range of concentration [µg/kg]	Reference Number
yl]ethanone				
9. Pesticides				
Aldrin	ng/g	10000.00	10000.00	[10]
Aldrin	ng/g	21.00-153.00	21.00-153.00	[30]
Chloropyrifos	ng/g	210.32	210.32	[31]
Cyclohexane isomers (lindane and others)	ng/g	5.0-8.2	5.0-8.2	[10]
DDT and related congeners	ng/g	13-22000	13-22000	[10]
Diazinon	ng/g	<LOD (14.6 ng/g)	<LOD (14.6 ng/g)	[31]
Dieldrin	ng/g	15-27000	15-27000	[10]
Dieldrin	ng/g	n.d.	n.d.	[30]
Endosulfans	ng/g	3.5-51000	3.5-51000	[10]
Endosulfans	ng/g	51.00-145.00	51.00-145.00	[30]
Endrin	ng/g	5.6-2800	5.6-2800	[10]
Endrin	ng/g	n.d.	n.d.	[30]
Heptachlor epoxides	ng/g	n.d.	n.d.	[30]
Heptachlor	ng/g	13-46000	13-46000	[10]
Isobenzan	ng/g	1.9-350	1.9-350	[10]
Isodrin		ND	ND	[10]
Permethrin isomers	µg/kg dw	143-671	143-671	[32]
Quintozene	ng/g dw	ND; 1.2-100	ND; 1.2-100	[10]
10. Phenols				
Nonylphenol (NPE)	mg/kg dm	50.00	0.05	[5]
NPE	mg/kg	39570.00	39570000	[33]
NPE	mg/kg	22048.00	22048000	[34]
NPE	mg/kg	14.3-3150.3	14300-3150300	[35]
Alkyphenols (nonyl and octylphenol)				
NP	µg/kg dw	0.01-1450	0.01-1450	[36]
NP	mg/kg	3.6-93	3600-93000	[37]
NP	µg/kg dw	142-500	142-500	[28]
Bisphenol-A (BPA)	µg/kg dw	70-770	70-770	[38]
4-hydroxybiphenyl	µg/kg dw	n.d.-12	n.d.-12	[38]
2-hydroxybiphenyl	µg/kg dw	63-172	63-172	[38]
PhenolSSL	mg/kg	<5	<5000	[39]
4-t-octylphenol	µg/kg dw	77-201	77-201	[38]
4-t-nonylphenol	µg/kg dw	25-17-3675	25-17-3675	[38]
4-chloro-3-methylphenol	µg/kg dw	14-40	14-40	[38]
4-chloro-2-methylphenol	µg/kg dw	n.d.	n.d.	[38]
2-t-butyl-4-methylphenol	µg/kg dw	n.d.	n.d.	[38]
11. Phthalate acid esters/plasticizers	mg/kg dm	100.00	100000	[5]
Bis(2-ethylhexyl)phthalat (DEPH)	mg/kg dw	122.09-1651.85	122090-1651850	[40]
Bis(2-ethylhexyl)phthalat (DEPH)	mg/kg	16.50	16500	[33]
Bis(2-ethylhexyl)phthalat (DEPH)	mg/kg	27-55	27000-55000	[34]

Parameter/ Compound	Unit	Reported range of concentration	Range of concentration [µg/kg]	Reference Number
Bis(2-ethylhexyl)phthalat (DEPH)	µg/l	28-122	28-122	[41]
Bis(2-ethylhexyl)phthalat (DEPH)	µg/kg dw	12-1110	12-1110	[36]
Bis(2-ethylhexyl)phthalat (DEPH)	mg/kg dw	47.13-1651.85	47130-1651850	[40]
Bis(2-ethylhexyl)phthalat (DEPH)	mg/kg dw	1.5-3513.8	1500-3513800	[35]
12. Polychlorinated di-benzo-dioxins and furans				
PCDD/F	ng TE/kg dm	100.00		[5]
PCDD	pg/g	0.62-673		[42]
PCDF	pg/g	0.46-104		[42]
PCDD	pg/g dw	1.00 - 22300		[43]
PCDF	pg/g dw	1.00 - 1000.00		[43]
PCDD	pg/g dw	2.04 - 51500		[44]
PCDF	pg/g dw	7.97 - 414000		[44]
PCDD/F	pg TE/g dm	12.00 - 29.00		[43]
PCDD/F	pg TE/g dm	19.9 - 225.00		[44]
PCDD/F	ng TE/kg dm	3.35 - 91.70		[45]
13. Polychlorinated biphenyls (PCBs)				
PCB	mg/kg dm	0.80	800	[5]
PCB	µg/g dw	1.31 - 1.63	1310-1630	[46]
PCB	mg/kg	43831.00	43831000	[39]
PCB	mg/kg	0.3-0.7	300-700	[47]
PCB	mg/kg dw	0.26-2.91	260-2910	[48]
PCB	mg/kg dw	0.010-0.192	10-192	[40]
PCB	ng/g	550.00	0.550	[6]
PCB	mg/kg	0.005-0.227	5-227	[35]
14. Polynuclear aromatic hydrocarbons				
Acenaphthene	mg/kg dry	<0.05	<50	[49]
Acenaphthene	µg/kg	nd; 44-492	nd; 44-492	[50]
Acenaphthylene	µg/kg	18-32	18-32	[51]
Acenaphthylene	µg/kg	18-118	18-118	[50]
Anthracene	µg/kg	61-234	61-234	[51]
Anthracene	µg/kg	34-292	34-292	[50]
Benzo(a)anthracene	µg/kg	64-184	64-184	[51]
Benzo(a)anthracene	µg/kg	29-184	29-184	[50]
Benzo[ghi]perylene	µg/kg	n.d.-43	n.d.-43	[51]
Benzo[ghi]perylene	µg/kg	nd; 21-589	nd; 21-589	[50]
Benzo[b]fluoranthene	µg/kg	33-52	33-52	[51]
Benzo[b]fluoranthene	µg/kg	19-479	19-479	[50]
Benzo[k]fluoranthene	µg/kg	17-49	17-49	[51]
Benzo[k]fluoranthene	µg/kg	nd; 6-289	nd; 6-289	[50]
Benzopyrene congeners	µg/kg	32-45	32-45	[51]
Benzopyrene congeners	µg/kg	17-522	17-522	[50]
Chrysene	µg/kg	67-177	67-177	[51]
Chrysene	µg/kg	13-312	13-312	[50]

Parameter/ Compound	Unit	Reported range of concentration	Range of concentration [µg/kg]	Reference Number
Dibenzoanthracene congeners	µg/kg	n.d.	n.d.	[51]
Dibenzoanthracene congeners	µg/kg	nd; 2-125	nd; 2-125	[50]
Fluoranthene	µg/kg	**56-629**	**56-629**	[51]
Fluoranthene	µg/kg	56-629	56-629	[50]
Fluorene	µg/kg	77-704	77-704	[51]
Fluorene	µg/kg	28-909	28-909	[50]
Indeno(1,2,3-pyrene	µg/kg	46-295	46-295	[51]
Indeno(1,2,3-pyrene	µg/kg	nd; 27-461	nd; 27-461	[50]
Naphthalene	µg/kg	nd; 27-309	nd; 27-309	[50]
Perylene	µg/kg	nd; 21-589	nd; 21-589	[50]
Phenanthrene	µg/kg	250-2030	250-2030	[50]
Pyrene	µg/kg	112-702	112-702	[50]
Pyrene (phenyl)	µg/kg	112-706	112-706	[51]
Total PAH	mg/kg dm	6.00	6000	[5]
PAH	µg/kg	1130-5520	1130-5520	[50]
PAH	µg/g dw	1.10 - 7.52	1.10 - 7.52	[46]
PAH	mg/kg	39479.00	39479000	[33]
PAH	mg/kg	39722.00	39722000	[39]
PAH	mg/kg	3.38-9.15	3380-9150	[34]
PAH	µg/l	0.05-3.40	0.05-3.40	[41]
PAH 16	mg/kg	14.6-30.6	14600-30600	[47]
PAH 9	µg/g dw	0.67- 2.55	670-2550	[46]
PAH	mg/kg	0.1-16	100-16000	[35]
PAH	mg/kg	0.01-0.31	10-310	[42]
PAH	µg/kg	51.9-4834.7	51.9-4834.7	[52]
PAH	mg/kg	0.21-2.67	210-2670	[53]
PAH	ng/g	386-6387	386-6387	[30]
PAH	ng/g	34-19.11	34-19.11	[52]
PAH	ng/g	31.5-137.6	31.5-137.6	[54]
15. Sterols, stanols and estrogens				
Cholesterol	µg/kg	210-5000	210-5000	[55]
Coprostanol	µg/kg	39722.00	39722.00	[55]
Estradiol (17b)	ng/l	2.40-3.00	0.0024-0.003	[20]
Estrone	ng/l	2.40-4.40	0.0024-0.0044	[20]
Ethinylestradiol (17a)	ng/l	<LOQ		[20]
16. Surfactants	mg/kg dm	2600.00	2600000	[5]
Alcohol ethoxylates	mg/kg d.m.	1.00-98.00	1000-98000	[56]
Linear alkylbenzene sulphonate (LAS)	mg/kg	< 50	<50000	[33]
Linear alkylbenzene sulphonate (LAS)	mg/kg	50-15000	50000-15000	[39]
Linear alkylbenzene sulphonate (LAS)	mg/l	5000-15000	5000000-15000000	[57]
Linear alkylbenzene sulphonate (LAS)	mg/kg	16.95-3335	16950-3335000	[58]
Linear alkylbenzene sulphonate (LAS)	mg/kg	110-2870	110000-2870000	[34]
Linear alkylbenzene sulphonate	mg/kg	230-6764	230000-	[53]

Parameter/ Compound	Unit	Reported range of concentration	Range of concentration [µg/kg]	Reference Number
(LAS)			6764000	
Coconut diethanol amides	mg/kg d.m.	0.09-10.5	90-10500	[56]
Coconut diethanol amides	µg/l	0.30-260	0.30-260	[59]
Poly(ethylene glycol)s	mg/kg d.m.	1.7-17.6	1700-17600	[56]
17. Triaryl/alkyl phosphate esters				
Tri-n-butylphosphate	ng/l	0.09-0.36	90-360	[60]
18. Organic halides absorbable ((AOX)				
Organic halides absorbable (AOX)	mg/kg dm	500.00	500000	[5]
Organic halides absorbable (AOX)	mg Cl/kg dw	302-704	302000-704000	[48]

The analyses of these literature results (Table 3) evidenced that some of the concentrations of organic pollutants exceeded the permissible dose as being indicated in the EU Working Document on Sludge. In this context, one needs to consider that test samples used for research purposes are often chosen, because they feature unusual, often high loads of the pollutants of interest.

From a spatial coverage point of view the occurrence of organic pollutants in the sludge is less described and documented as for heavy metals. This has many reasons, the complexity of the analytical methods necessary for an accurate and precise analysis being certainly not the least one.

Indeed, also the main European and national pieces of legislation dealing with sewage sludge and waste water are focusing more on inorganic pollutants and various sum parameters. In addition, most of the organics are not persistent and usually it is believed that most of the organics are eliminated from sludge-treated soil via natural mechanisms. The "*non-detectability*" of a compound, which may undergo a quick first modification of a functional group, but then stays in soil in a modified form, may invite to this conclusion.

However, it is well known that the occurrence of organic pollutants in soil is stemming from a deliberate or accidental release following human activities [**61**]. For some of them, it is also known that they can appear in soil in natural ways [**62**]. Since their pathways in soil is strongly influenced by their polarity and hence the adsorption behaviour and depends consequently on the chemical structures and properties in addition to the soil properties [**63**, **64**].

2.2 Parameters influencing the concentration levels of organic pollutants in sewage sludge and in amended soil areas

The biodegradation process of organic pollutants starts in the wastewater treatment plants (WWTP) or in the sludge treatment plants (STP) in the bioreactors, with activated sludge. Consortia of the microorganisms, oxic or anoxic condition influence directly the conversion of the organic pollutants and the final chemical products appear after the process. Concentration of the organic compounds in the sewage sludge or wastewater depends on the size of the urban agglomeration where WWTP and STP are placed as well as on the year's season. During the winter when in many places the temperature does not exceed 5°C the microorganisms do not provide intensive processes as observed during summer.

Most of the studies providing on the biodegradation of organic pollutants report the conversion of toxic compounds by soil microorganisms. Naturally existing consortia provide the process mainly in anaerobic condition using the chemical molecules as the source of

carbon and energy. Some of the pollutants are more resistant for the biodegradation like PCDD and their half-lives are reported since 30 up till 170 years while the others are degraded in a few days as LAS, since 3 up till 7 days.
Many physico-chemical parameters like temperature, humidity or soil structure decide about the microbial degradation process of organic pollutants in soil. Water solubility or partition coefficients (e.g. K_{ow}) are useful in the estimation of run-off time of chemical compounds in soil and the risk of groundwater pollution.
For example adsorption of polychlorinated biphenyls to soil particles depends on the number of chlorine atoms in the congeners. It was observed that high chlorinated congeners with a higher log K_{ow} are adsorbed stronger to the terrestrial organic matter than less chlorinated congeners with lower water- octanol partition coefficient [**65**, **66**].

Table 3 Log K_{ow} values found in literature for chosen organic pollutants

Compounds	***Log K_{ow}***	***References***
Polychlorinated biphenyls (PCB):		
2,4,4'-triCB	5.80	[65]
2,2',5,5'- tetraCB	6.10	[65]
2,2',4,5,5'- pentaCB	6.40	[65]
2,2',4,4',5,5'-hexaCB	6.70	[65]
2,2',3,4,4',5,5'-heptaCB	6.90	[65]
2,2',3,3',4,4',5,5',6,6'-decaCB	7.36	[65]
a-Endosulfan	3.55	[**67**]
Aldrin	5.1	[67]
Isodrin	5.1	[67]
Dieldrin	4.6	[67]
Endrin	4.6	[67]
Heptachlor	5.4	[**68**]
Antibiotics:		
Gemfibrozil	4.77	[**69**]
Ibuprofen	3.97	[69]
Naproxen	3.18	[**70**]
Salicylic acid	1.19; 2.26	[69]; [70]

2.3 Case study: PCDD/F and dioxin-like PCB in amended soils since 1962

Concerning polychlorinated dibenzodioxins and furans (PCDD/Fs) and dioxin like polychlorinated biphenyls (DL-PCBs), a recently published study provides data on the resulting concentration on polychlorinated dibenzodioxines and dibenzofurans (PDCC/F) and dioxin-like polychlorinated biphenyls (DL-PCBs) in the soil columns as a result of different type of fertilizers [**71**]. In the long-term field experiment established in 1962, the influence of the application of biowaste-derived fertilizers such as sewage sludge (SLL), compost (COM) and farmyard manure (FYM) to a luvisol derived from loess on the contents of PCDD/Fs and DL-PCBs was studied. Control plots amended only with mineral fertilizer served as basis to compare the biowaste-amended soils with soils affected only by atmospheric deposition, thus experimentally separating the two pathways of soils contamination. Samples of the soil column down to a depth of 90 cm were taken in 2001 and analysed for PCDD/Fs and dioxin-like PCBs according to US-EPA methods 1613 and 1618, respectively.

2.4 Reflection on sludge land spreading

During the monitoring of organic chemicals concentrations in sludge the benefits and disadvantages of the agriculture use should be analysed. Sewage sludge contains many pollutants both organic and inorganic, nevertheless it can also be a sources of desirable compounds or elements i.e. phosphorus and nitrogen. Both, sludge and wastewater, can be used as natural fertilizers that replace industrial products. Phosphorus and nitrogen concentrations influence directly on the food and feed qualities [**73**, **74**, **75**].

Two European directives concern the concentrations and environmental disposal of phosphorus and nitrogen. Urban Waste Water Treatment Directive 91/271/EEC regulates the requirements concerning the sewage sludge disposal demanding not exceed the concentrations of total nitrogen and total phosphorus in sewage sludge more than 2 mg/l and 15 mg/l respectively [**79**]. Directive 91/676/EEC defines the water protection against nitrates as the pollutants origins from agriculture [**80**]. It is proposed to spread nitrogen with sewage sludge or manure not more than 170 kg per hectare each year.

The nutrients' content of sludge depends on its type as urban or industrial. The consortia of microorganisms that appeared in the plant tanks decide directly about the final nitrate forms of the effluents. Primary sludge consists mostly of the organic nitrogen forms [**81**], which during the biological processes are converted to various inorganic compounds. Also for phosphorus a chemical form decides about solubility and availability from the fertilizers. Different metals (iron, aluminium, calcium) that appear in sludge have significant influence on the phosphorus concentration and its availability after land application [**82**, **83**]. Such an effect can be observed in presence of mixture of iron, calcium and aluminium oxides, which remove over 90% of phosphate from effluent and then from groundwater in 4 years [**84**].

The year's seasons and geographical positions of the spread lands play an important role in the management of the sludge application to the fields. It is necessary to keep the proper balance between the nutrients' concentration and avoid the risk of nutrient leaching. During the summer the high mineral nitrogen content sludge should be avoided in the regions where the intensive rainfall and runoff are observed (Mediterranean regions). In such areas the soil structure also has an influence on the nutrients achievement in terrestrial ecosystem [**85**].

In many rivers phosphorus concentration is limited and depends on its source, transportation and storage [**86**]. Type of the soil affects flow and higher concentration of nutrients in the groundwater and rivers [**87**]. It also makes more effective a natural mineralization process, which is greater in a soil of light texture, amended by sludge treated aerobically. The nutrient enrichment effect in rivers appears during the vegetation period of plants or alga [**88**, **89**]. It must be taken into account that in the summer flow of the nutrients in soil is lower and biological activity is higher [**90**,**91**]. The equable process of nutrients' concentrations in such

area becomes impossible, which is one of the reasons why monitoring as well as a proper land management is required [**92**].

3 Pan-European Screening of Sewage Sludge Samples

3.1 Description of the campaign and selection of sampling sites

The initiative aimed at obtaining an EU-wide perspective on the occurrence of emerging pollutants in sewage sludge samples from WWTP receiving typical influents from European Cities and where sludges are possibly designated to agricultural use. Following its scheme of EU-wide monitoring exercises [**93**], JRC fully organized the centralized collection of sixty-one sewage sludge samples.

JRC asked for samples from WWTPs complying with the following characteristics:

- Type A (assessment of the pollutants originating from private households): These sites comprise a rural catchment, have no industry and very few craft industry in the catchment and feature a separate sewer system (domestic wastewater only).
- Type B (assessment of the pollutants originating from private households and runoff): These sites comprise a rural catchment, have no industry and very few craft industry in the catchment, and feature a combined sewer system (domestic wastewater and storm water).
- Type C (assessment of the pollutants originating from private households, urban runoff as well as from industry and craft industry): These sites comprise a predominantly urban catchment, have industry and craft industry in the catchment and feature a combined sewer system (domestic wastewater and storm water).

In order to facilitate the collaboration with the WWTPs, a clear mandate e.g. from the responsible Commission service to the JRC was needed. This mandate clearly guaranteed that the obtained results would have not be used to "judge" the performance of a given WWTP, but aimed at the compilation of knowledge on emerging organic contaminants that may pose a problem.

All the EU countries were contacted via their permanent representatives at the Commission in Brussels. Furthermore, Switzerland participated on the basis of previous exercises and JRC used its own contacts in drawing the map of participating sites. The contribution of each country to the campaign is summarised in the table below.

Table 4 Contribution of EU countries

Country	***Number of samples WWTPs***
Austria	2
Belgium	9
Czech Republic	2
Finland	6
Germany	6
Greece	3
Hungary	1
Ireland	2
Lithuania	3
Portugal	2
Romania	1
Slovenia	1
Sweden	8
Switzerland	9
The Netherlands	6

Each participant was asked to compile the accompanying documentation (i.e.: sampling bill) with the following relevant information:

- Country Address
- River basin receiving effluent
- Geographic coordinates (WGS84)
- Sampling date/time
- Attachments (possible photos, SOPs, or further information deemed useful)
- Contact person for all dispatch issues
- Sampling operation/Sampling method
- Field observations and weather
- Other observations
- Field analyses
- Relevant information about the plant.

Although not all participants provided the requested complete information at the time this report was finalised, a good documentation state was achieved. The most relevant information about the collected samples is summarised in Table 5.

For reasons of confidentiality the geographic coordinates, present in all cases, is not disseminated in this report.

Table 5 - Relevant information on FATE-SEES collected samples

Location code	***Sampling Date***	***Sampling Time***	***Weather conditions***	***Sludge sampling operations***	***Discharges Type***	***Plant capacity***	***Capacity population equivalent (PE)***	***Other information***
Austria								
0043-SLF-275-01-00	17/03/2011	10:50	Raining/ 7˚C	Grab samples			138150	Activated sludge tank, anaerobic sludge digestion. Designed for carbon removal, nitrification and denitrification, phosphorous precipitation. Important indirect dischargers: metal, food, landfill, textile, laundry
0043-SLF-276-01-00	16/03/2011	16:35	Cloudy/ 10˚C	Grab samples			380000	Two stage activated sludge plant, anaerobic sludge digestion. Designed for carbon removal, nitrification and denitrification, phosphorous precipitation. Strongly influenced (COD) from one indirect discharger (paper industry). Other important dischargers: food, metal, textile.
Belgium								
0043-SLF-263-01-00	11/3/2011	9:00	Cloudy/ 9˚C	Grab samples			200000	Grab taken at the centrifugation exit from a small heap.
0043-SLF-264-01-00	16/03/2011	9:00	Sunny/ 10˚C	Grab samples		?	?	Grab taken at the centrifugation exit with adapted shovel.
0043-SLF-265-01-00	16/03/2011	11:00	Sunny/ 11˚C	Grab samples		?	?	6 bottles taken just before the secondary sedimentation, two other bottles taken from the primary treatment output tank.
0043-SLF-266-01-00	10/3/2011	15:00	Cloudy/ 11˚C	Grab samples		?	?	Samples taken at the press exit with an adapted shovel.
0043-SLF-267-01-00	16/03/2011	10:00	Sunny/ 10˚C	Grab samples		?	?	Grab taken at the centrifugation exit with adapted shovel.
Czech Republic								
0043-SLF-326-01-00	9/6/2011	8:00	Raining/ 18˚C	Grab samples	Municipal, rain and industrial waters	50000000 m^3/year	513000	Mechanical and biological treatment (nitrification and denitrification zone, too), phosphorous is precipitated chemically by iron sulphate

Location code	*Sampling Date*	*Sampling Time*	*Weather conditions*	*Sludge sampling operations*	*Discharges Type*	*Plant capacity*	*Capacity population equivalent (PE)*	*Other information*
0043-SLF-327-01-00	9/6/2011	7:30	Raining/ 18˚C	Grab samples	Municipal, rain and industrial waters	1525816	25000	Mechanical and biological treatment (nitrification and denitrification zone, too), phosphorous is precipitated chemically by iron sulphate. Sludge is pressed and stored before main microbial thermophilic reactions. In the main reactor sludge is wormed by oxygen up to 58˚C and hygenize by the microbial processes. After hygenization the sludge is ready to be used in agriculture
Finland								
0043-SLF-269-01-00	11/4/2011	9:30	Cloudy	Grab samples			16614	
0043-SLF-270-01-00	12/4/2011	11:00	Cloudy	Grab samples			20211	
0043-SLF-271-01-00	12/4/2011	8:00	Cloudy	Grab samples			9897	
0043-SLF-272-01-00	12/4/2011	9:00	Cloudy	Grab samples			1222140	
0043-SLF-273-01-00	11/4/2011	13:00	Cloudy	Grab samples			432432	
0043-SLF-274-01-00	11/4/2011	10:30	Cloudy	Grab samples			3037	
Germany								
0043-SLF-283-01-00	7/4/2011	8:10	Cloudy/ 14˚C	Grab samples		1000000	970000	over 30% industry
0043-SLF-288-01-00	n.a.	n.a.	Cloudy/ 17˚C	Grab samples			300000	Municipal wastewater treatment plant, marginal influence of industry. Drainage system: chamber filter press, addition of ferric-II chloride, calcium carbonate. Treatment: mesophilic anaerobic sludge digestion. Wastewater treatment: active sludge process.
0043-SLF-289-01-00	n.a.	n.a.	Cloudy/ 17˚C	Grab samples			45000	Municipal wastewater treatment plant, marginal influence of industry. Drainage: centrifuge, addition of calcium carbonate. Treatment: mesophilic anaerobic sludge digestion. Wastewater treatment: active sludge process.

Location code	*Sampling Date*	*Sampling Time*	*Weather conditions*	*Sludge sampling operations*	*Discharges Type*	*Plant capacity*	*Capacity population equivalent (PE)*	*Other information*
0043-SLF-290-01-00	11/4/2011	n.a.		Dry weather	Grab samples		7000	Activated sludge plant with aerobic sludge stabilization
0043-SLF-291-01-00	20/04/2011	8:45		Sunny	n.a.	40000	27104	
0043-SLF-302-01-00	7/4/2011	8:00		Sunny/ 9˚C	Composite samples			
Greece								
0043-SLF-277-01-00	3/5/2011	8:00		Cloudy/ 20˚C	Grab samples		1333000	Only municipal. The main plant treating ww of the second biggest city of Greece.
0043-SLF-278-01-00	3/5/2011	11:30		Cloudy/ 20˚C	Grab samples		91767	Some rainfall, sludge not covered. WW of the touristic area of Thessaloniki. Mainly municipal.
0043-SLF-279-01-00	3/5/2011	9:35		Raining/ 20˚C	Grab samples		15000	Covered sludge not affected by rain. Industrial sewage effluent from the nearby industrial area.
Hungary								
0043-SLF-293-01-00	18/04/2011	7:00		Sunny	Grab samples			
0043-SLF-294-01-00	18/04/2011	7:50		Sunny	Grab samples			
					Ireland			
0043-SLF-295-01-00	11/4/2011	11:15		Sunny/ 10˚C	Grab samples		84114	
0043-SLF-296-01-00	7/4/2011	9:00		Cloudy	Grab samples		1740000	is a tertiary plant with primary, biological and UV treatment during the summer months. The samples have gone through hydrolysis, digestion and thermally dried at 450 °C
Lithuania								
0043-SLF-260-01-00	7/3/2011	14:05		Sunny/ 2˚C	Grab samples		100000	Home and industrial wastewater.
0043-SLF-261-01-00	7/3/2011	14:00		Sunny/ 1˚C	Grab samples		150000	Sample taken after centrifugation.
0043-SLF-262-01-00	7/3/2011	12:00		16˚C			244500	Samples taken inside the building according to ISO 5667-13:1997. Plant has elimination of nitrogen and phosphorous.
Portugal								
0043-SLF-314-01-00	12/5/2011	11:00		Sunny	Grab samples			

Location code	*Sampling Date*	*Sampling Time*	*Weather conditions*	*Sludge sampling operations*	*Discharges Type*	*Plant capacity*	*Capacity population equivalent (PE)*	*Other information*
0043-SLF-313-01-00	19/05/2011	11:00		Sunny	Grab samples			
Romania								
0043-SLF-259-01-00	8/3/2011	10:45		Sunny/ 1˚C	Grab samples		320000	Sampled the fraction used for agricultural soil. The sludge was stored in piles in order to be dried. The samples were collected from different points of the pile depth, SR EN ISO 5667-13:2000
Slovenia								
0043-SLF-268-01-00	11/3/2011	n.a.		n.a.	Composite samples		360000	Subsamples of dried anaerobically stabilized sludge were collected every 3 hours, 5 days a week from 1.1-30.10.2010. 10 months composite sample. The sample is dried anaerobically stabilized sludge.
Sweden								
0043-SLF-305-01-00	27/06/2011	10:35		Cloudy/ 18.6˚C	Grab samples		876988	
0043-SLF-306-01-00	15/06/2011	7:00		Sunny	Grab samples	900000	656000	Large WWTP processing industry sewage (mix) and household sewage. Hospital, laundry, food and craft industry connected
0043-SLF-307-01-00	14/06/2011	n.a.		Cloudy/ 16˚C	Grab samples	60000	27332	Medium sized WWTP processing small industry sewage and household sewage. Laundry is connected
0043-SLF-308-01-00	14/06/2011	10:00		Cloudy/ 14˚C	Grab samples	116000	128699	Medium sized WWTP processing small industry sewage and household sewage. Hospital, dairy is connected.
0043-SLF-309-01-00	15/06/2011	10:30		Cloudy	Grab samples	110000	73257	Medium sized WWTP processing industry sewage (mix) and household sewage. Hospital, laundry, food and craft industry connected
0043-SLF-310-01-00	16/06/2011	11:00		Sunny/ 18˚C	Grab samples	330000	74405	Medium sized WWTP processing mixed industry sewage and household sewage. Laundry and craft industries are connected
0043-SLF-311-01-00	13/06/2011	14:00		Cloudy/ 23˚C	Grab samples	60000	25362	Medium sized WWTP processing (small) industry sewage and household sewage. Hospital connected

Location code	*Sampling Date*	*Sampling Time*	*Weather conditions*	*Sludge sampling operations*	*Discharges Type*	*Plant capacity*	*Capacity population equivalent (PE)*	*Other information*
0043-SLF-312-01-00	14/06/2011	10:00		Raining/16˚C	Grab samples	6500	2466	Small sized WWTP, processing household sewage
Switzerland								
0043-SLF-325-01-00	7/6/2011	na		Sunny/ 18˚C	Composite samples		630	
0043-SLF-322-01-00	7/6/2011	13:30		Sunny/ 18˚C	Grab samples		600000	
0043-SLF-319-01-00	7/6/2011	11:00		Sunny/ 18˚C	Grab samples		10000	
0043-SLF-316-01-00	7/6/2011	10:00		Sunny/ 18˚C	Grab samples		37500	
0043-SLF-321-01-00	7/6/2011	13:30		Sunny/ 18˚C	Grab samples		19750	
0043-SLF-320-01-00	8/6/2011	13:30		Raining/ 18˚C	Grab samples		32000	
0043-SLF-318-01-00	8/6/2011	10:30		Cloudy/ 18˚C	Grab samples		1067	
0043-SLF-323-01-00	8/6/2011	9:30		Cloudy/ 18˚C	Composite samples		500	
0043-SLF-317-01-00	8/6/2011	8:00		Cloudy/ 18˚C	Grab samples		383	
The Netherlands								
0043-SLF-282-01-00								
0043-SLF-285-01-00	11/4/2011	n.a.		Sunny/ 19˚C	Grab samples		113500	
0043-SLF-286-01-00	5/4/2011	9:00		Cloudy/ 15˚C	Grab samples	1300000	90000	the sludge destination is incineration and not applied on agricultural soils
0043-SLF-287-01-00								
0043-SLF-292-01-00	11/4/2011	n.a.		n.a.	Grab samples		30000	
0043-SLF-303-01-00	10/5/2011	10:00		Sunny/ 20˚C	Composite samples	200000	160000	Sample taken from the membrane filter press after sludge digestion and dewatering. BioP installation and struvite formation to lower phosphate concentration in filter water. Struvite is still in sludge, not separately collected.
0043-SLF-304-01-00	3/5/2011	11:10		Sunny/ 12˚C	Grab samples	300000	250000	Sludge collected before additives are added.

A sewage sludge sample inventory was build up at JRC for sample distribution, analytical processing and data coordination. Data were registered in the IES Environmental Laboratory Data Information Management System, which allowed also retrieving the data on a geo-referenced basis.
Upon completion of analyses, the samples were stored in the IES Sample Archive in case that a need for further characterisation arises. Since this was an action limited in time, the size of the archive remains manageable.
As mentioned previously, exact location and origin of the sludge samples is confidential and will not be disseminated. In addition, the data could be compared with the earlier collected data obtained from the European cities or data to be derived from Environmental Specimen Banks.

3.2 Experimental methods

3.2.1 Sample preparation

Sludge samples were freeze-dried using a GAMMA 1-16 LSC (Christ) instrument in order to reduce water content. After that samples were homogenized and ground in an agate ball mixer mill to reduce particle size to a maximum of 630µm.

3.2.2 Microwave-assisted digestion

A Multiwave 3000 microwave (Anton Paar) device was employed for samples digestion. PrEN Standard 16174 was used [**94**]. About 0.1 g of each sample (soil, sludge, compost and CRMs) was weighted and introduced into a high-pressure, closed, Teflon decomposition vessel. The mixture of 1.5 millilitres of HNO_3 and 4.5 mL of HCl (*i.e.* a defined mixture known as *'aqua regia'*) were carefully added to each sample and the vessels were gently shaken, sealed and digested in microwave oven under previously optimized operating conditions. Blank solutions were prepared by applying the same procedure and reagent solutions without sample.
The microwave autoclave can simultaneously digest up to 48 samples in the reaction chamber under identical experimental conditions. The maximum pressure of the reaction chamber with sample vessels inside was set to 1225 bar. Then the vessels were heated in the microwave autoclave for 35 min reaching a temperature of maximum 140°C and a pressure of approximately 20 bar. The pressure and temperature were monitored during all the analysis by the use of a T/P (Temperature/Pressure) sensor. Before opening the reaction chamber, the digests were allowed to cool for about 180 min to well below the boiling point of the acid mixture at atmospheric pressure.
Each extract was filtered in a 50 mL glass flask using a clean glass funnel and a Minisart RC 25 filter. The vessel and the vessel cup were subsequently rinsed three times with Milli-Q water and the rinse water was filtered in the same flask. At the end, the flask was completed to volume. The resulting samples were stored at 4 ºC until analyses.

3.2.3 Heavy Metals by ICP-AES

Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) was used. The method was following prEN 16170 [**95**], which was fully implemented for the analysis of sludge samples in JRC laboratories and hence validated accordingly. Validation of the horizontal standard was done using Certified Reference Materials (CRMs): BCR 141R '*Calcareous Loam Soil*', BCR 142 '*Light Sandy Soil*', SRM 2789 "*San Joaquin Soil*" and LCG 6181 '*sewage sludge*'.
The calibration curves, detection and quantification limits, trueness as well as repeatability

were determined. An expanded uncertainty was calculated.
For ICP analysis an aliquot of the digested samples was transferred to the ICP sample vials. The following elements were determined: Ag, Al, As, Ba, Cd, Co, Cr, Cu, Fe, Mg, K, Mn, Mo, Ni, P, Pb, Sb, Se, Ti, V and Zn. The low calibration range was from 0.02 to 0.5 mg/L. The high calibration range was from 0.5 to 5 mg/L. The performance characteristics of the methods are listed in Table 6, Table 7 and
Table 8, respectively.
In order to estimate LoD (Limit of Detection) and LoQ (Limit of Quantification), samples containing the selected elements at very low concentration, were analysed. When an element was non available in the sample, a blank was used. The following formulas were used to compute LoD and LoQ:

$$LOD = \Phi_{n,\alpha} \cdot \frac{s_L}{b}$$

$$LOQ = k \cdot \Phi_{n,\alpha} \cdot \frac{s_L}{b}$$

where s_L is the standard deviation of the ten replicates and b is the slope of the used calibration curve. $\Phi_{n,\alpha}$ is a multiplier factor that takes into account the probability that certain response could be due to the standard deviation of the blank rather than the one of the analyte. The factor *k* corresponds to the reciprocal value of the desired accuracy.
For 10 measurements and at a 95% confidence level ($\alpha = 0.05$) the $\Phi_{n\,\alpha}$ factor is equal to 1.9. LOQ is computed using a *k* factor of 2, which give a 50% of accuracy.

Table 6 - LoD and LoQ (expressed in mg/L) for the selected heavy metals in sludge samples. For the elements Ba, Mn, Se and Ti, a blank was used for the computation.

	LOD	***LOQ***		***LOD***	***LOQ***
Ag	0.06	0.12	*Mo*	0.36	0.72
Al	1.53	3.06	*Ni*	0.14	0.27
As	2.63	5.25	*Pb*	1.26	2.52
Ba	0.02	0.04	*Sb*	1.66	3.32
Cd	0.09	0.18	*Se*	1.78	3.56
Co	0.18	0.35	*Ti*	0.03	0.05
Cr	0.16	0.32	*V*	0.81	1.62
Cu	0.19	0.38	*Zn*	2.12	4.23
Fe	6.66	13.32	*P*	3.03	6.06
Mg	3.58	7.15	*K*	4.83	9.66
Mn	0.02	0.03			

Table 7 - Average recoveries for the selected heavy metals obtained in sludge samples

	LOW	*HIGH*		*LOW*	*HIGH*
Ag	101%	92%	*Mo*	87%	92%
Al	-	103%	*Ni*	97%	96%
As	83%	90%	*Pb*	94%	97%

Ba	89%	95%	*Sb*	101%	91%
Cd	95%	88%	*Se*	83%	92%
Co	98%	89%	*Ti*	90%	92%
Cr	96%	98%	*V*	99%	93%
Cu	93%	99%	*Zn*	-	89%
Fe	-	98%	*P*	-	122%
Mg	-	96%	*K*	-	102%
Mn	87%	92%			

Table 8 - Expanded uncertainty of ICP-OES determination (expressed in %)

	LOW	*HIGH*		*LOW*	*HIGH*
Ag	4.5%	6.2%	*Mo*	3.9%	3.5%
Al	-	7.2%	*Ni*	6.0%	2.6%
As	6.3%	4.0%	*Pb*	6.9%	2.3%
Ba	6.1%	6.7%	*Sb*	5.5%	10.1%
Cd	5.6%	5.5%	*Se*	3.3%	9.3%
Co	7.1%	5.0%	*Ti*	8.3%	10.5%
Cr	6.0%	1.3%	*V*	5.3%	4.0%
Cu	3.0%	5.8%	*Zn*	-	4.0%
Fe		5.2%	*P*	-	8.6%
Mg		7.9%	*K*	-	7.7%
Mn	3.9%	6.9%			

3.2.4 Could Vapour-Atomic Adsorption Spectrometry (CV-AAS) analysis

The determination of Hg was carried out by Cold Vapour-Atomic Absorption Spectrometry (CV-AAS) technique using an Advanced Mercury Analyser instrument (AMA 254, Altec). Samples were measured directly after lyophilisation and grinding without further treatment.
The method for Could Vapour-Atomic Adsorption Spectrometry (CV-AAS) was fully validated and implemented in the analysis of sludge samples. The methods was validated using Certified Reference Materials (CRMs): BCR 141R '*Calcareous Loam Soil*', BCR 142 '*Light Sandy Soil*', SRM 2789 "*San Joaquin Soil*" and LCG 6181 '*sewage sludge*'.
The calibration curves, detection and quantification limits, trueness as well as repeatability were determined. An uncertainty budget was determined.

Table 9 CV-AAS operational conditions

Parameter	
Drying time	60s
Decomposition time	200s
Cuvette clear time	45s
Delay	0s
Cell to use for analysis	Low / High cell
Metric to use for calculation	Peak area

The low calibration range was from 0.05 to 0.5 mg/L. The high calibration range was from 0.5 to 5 mg/L. LoD and LoQ were obtained following the same approach as in case of ICP-AES measurements. Due to the non-availability of a soil, sludge and compost sample containing Hg at very low concentration, a blank was used instead. Ten replicates were made in order to compute the standard deviation. The following values were observed: *LOD = 4 µg/L* and *LOQ= 8 µg/L.*
Low recoveries were computed using the following certified reference materials (CRMs): BCR 141R *calcareous loam soil* (0.25mg/kg Hg) and BCR 142R *Light sandy soil (*0.067mg/kg Hg). For method validation, CRMs were analysed in triplicate for five different days. Results are presented below.

Table 10 Results of replicate analysis of CRM BCR 141R and 142R

	Day 1	*Day 2*	*Day 3*	*Day 4*	*Day 5*	***Average***
BCR 141R	113%	103%	103%	104%	108%	**106%**
BCR 142R	107%	96%	95%	99%	106%	**101%**

For the *high recovery* the CRMs: SRM 2789 *San Joaquin Soil* (4.9 mg/kg Hg) and LCG 6181 (1.4 mg/kg Hg) were used. The results are presented hereafter.

Table 11 Results of replicate analysis of CRM LCG 618 and SRM 2789

	Day1	*Day 2*	*Day 3*	*Day 4*	*Day 5*	***Average***
LCG 6181	110%	122%	117%	120%	115%	**117%**
SRM 2789	118%	120%	106%	109%	111%	**113%**

In order to take into account a confidence level, the combined uncertainty is to be multiplied by a coverage factor, *k*, to produce the expanded uncertainty. The choice of this factor was

done taking into account a 95% confidence level, which give a coverage factor of 2. The expanded uncertainty is given by:

$$u_{expanded} = k \cdot u_{combined}$$

To compute the expanded uncertainty we chose the higher combined uncertainty in both low and high calibration. In percentage terms, we obtain an expanded uncertainty of 7% in low calibration and 8% in high calibration.

3.2.5 Polycyclic musk compounds

A gas chromatography coupled to mass spectrometric detection (GC-MS) for the determination of polycyclic musk compounds (PCMs) in sewage sludge samples was developed.

3.2.5.1 Sample preparation for PCM

The method was developed for the analysis of the following compounds: cashmerane, celestolide, phantolide, traesolide galaxolide and tonalide. After addition of an internal standard (deuterated tonalide and hexachlorbenzene-C^{13}) the samples (1 g) were extracted with 20 mL ethanol/sodium acetate puffer. Additionally 400 µL DEA-DDC (diethyl-ammonium-diethyl-dithiocarbamate) were added as a complexing agent. The samples were shaken overhead for about 2.5 hours. After addition of 20 mL n-hexane the samples were shaken for another 60 minutes. The extracts were centrifuged for a better phase separation (3000 U/min, 5min) and the hexane phase was separated. After another extraction with 5 mL of n-hexane, the organic phase was evaporated to approx. 5 mL and a clean up step was performed with aluminium oxide (2 g deactivated by baking at 400 °C for 4 hours and activated with 10 % water). The analytes were eluted by a mixture of n-hexane/ethyl acetate (90:10,v:v). The extracts were evaporated to less than 900 µL with a gentle stream of nitrogen. After addition of an injection standard the extracts were filled up to a final volume of 1 mL and an aliquot (1 µL) is injected into a GC-MS system. The substances were detected using the EI-GC-MS in the SIM mode.

3.2.5.2 GC-MS analysis

The operating conditions for GC-MS analysis are reported below:

Table 12 – Conditions for PCM measurements by GC-MS

Column: J&W DB5-MS Nominal length 60m Nominal Diameter 0,25 mm Nominal film thickness 0,25 µm Mode constant flow Initial flow 1,5 mL / min Helium			
Oven Initial Temperature 40°C Initial Time 1’ Ramps: 6°c/min up to 120°C 10°C/min up to 330°C hold for 3 min.	#	Rate	Final Temp Final Time

Run Time 38 min	
Front Inlet Mode splitless Initial Temperature 260 °C Pressure -- Purge Flow -- Purge Time -- Total Flow 1,5 mL/min Gas saver -- Gas Type Helium	Initial Temperature 260 °C Equilibration Time 1 ‘ Initial Time -- Rate -- Final Temp -- Hold Time --
MS Quad (℃) not heated	
MS Source (℃) 255 °C	

3.2.5.3 Performance characteristics

Performance characteristics for the method are displayed for the individual compounds in Table 13 to Table 15.

Table 13 LoD and LoQ (expressed as µg/kg d.m.) of PMC determination by GC-MS

	Cashmerane	*Celestolide*	*Phantolide*	*Traesolide*	*Galaxolide*	*Tonalide*
LOD	5	7.5	5	5	10	5
LOQ	10	15	10	10	20	10
Recovery	84%	91%	85%	87%	81%	80%
Est. Uncertainty	26%	29%	18%	24%	22%	17%

Table 14 Recoveries of PMCs

	Cashmerane	*Celestolide*	*Phantolide*	*Traesolide*	*Galaxolide*	*Tonalide*
Recovery	84%	91%	85%	87%	81%	80%
Est. Uncertainty	26%	29%	18%	24%	22%	17%

Table 15 Estimated uncertainty of PCMs determination

	Cashmerane	*Celestolide*	*Phantolide*	*Traesolide*	*Galaxolide*	*Tonalide*
Est. Uncertainty	26%	29%	18%	24%	22%	17%

3.2.6 Siloxanes

3.2.6.1 Sample preparation

The method was developed for the analysis of the following compounds: cashmerane, celestolide, phantolide, traesolide galaxolide and tonalide. After addition of an internal standard (tetrachlorbenzene $^{13}C_6$) the samples (1 g) were extracted with 20 mL ethanol/sodium acetate puffer. Additionally 400 µL DEA-DDC (diethyl-ammonium-diethyl-dithiocarbamate) was added as a complexing agent. The samples were shaken overhead for about 2.5 hours. After addition of 20 mL n-hexane the samples were shaken for another 60 minutes. The extracts were centrifuged for a better phase separation (3000 U/min, 5min) and the hexane phase was separated. After another extraction with 5 mL of n-hexane, the organic phase was evaporated to approx. 5 mL and a clean-up step was performed with aluminium oxide (2 g deactivated by baking at 400 °C for 4 hours and activated with 10 % water). The analytes were eluted by a mixture of n-hexane/ethyl acetate (90:10,v:v). The extracts were evaporated to less than 900 µL with a gentle stream of nitrogen. After addition of an injection standard, the extracts were filled up to a final volume of 1 mL and an aliquot (1 µL) was injected into a GC-MS system. The substances were detected using the EI-GC-MS in the SIM mode.

3.2.6.2 GC-MS analysis

The operating conditions for GC-MS analysis are reported below.

Table 16 - Conditions for siloxane measurements by GC-MS

Column: J&W DB5-MS Nominal length 60m Nominal Diameter 0,25 mm Nominal film thickness 0,25 µm Mode constant flow Initial flow 1,5 mL / min Helium	
Oven Initial Temperature 40°C Initial Time 1' Ramps: 6°c/min up to 120°C 10°C/min up to 330°C hold for 3 min. Run Time 38 min	# Rate Final Temp Final Time
Front Inlet Mode splitless Initial Temperature 260 °C Pressure -- Purge Flow -- Purge Time -- Total Flow 1,5 mL/min Gas saver -- Gas Type Helium	Initial Temperature 260 °C Equilibration Time 1 ' Initial Time -- Rate -- Final Temp -- Hold Time --
MS Quad (°C) not heated	
MS Source (°C) 255 °C	

3.2.6.3 Performance characteristics

Performance characteristics of the method are displayed in the table below.

Table 17 LoD and LoQ (expressed as µg/kg d.m) of siloxanes determination by GC-MS

	Octamethyltrisiloxan (MDM)	*Octamethylcyclotetrasiloxan (D4)*	*Decamethyltetrasiloxan (MD2M)*	*Decamethylcyclopentasiloxan (D5)*	*Dodecamethylpentasiloxan (MD3M)*	*Dodecamethylcyclohexasiloxan (D6)*
LOD	5	30	5	30	5	60
LOQ	10	60	10	60	10	120

Table 18 Recovery of siloxanes

	Octamethyltrisiloxan (MDM)	*Octamethylcyclotetrasiloxan (D4)*	*Decamethyltetrasiloxan (MD2M)*	*Decamethylcyclopentasiloxan (D5)*	*Dodecamethylpentasiloxan (MD3M)*	*Dodecamethylcyclohexasiloxan (D6)*
Recovery	71%	77%	86%	91%	85%	90%

Table 19 Estimated uncertainty of siloxanes determination

	Octamethyltrisiloxan (MDM)	*Octamethylcyclotetrasiloxan (D4)*	*Decamethyltetrasiloxan (MD2M)*	*Decamethylcyclopentasiloxan (D5)*	*Dodecamethylpentasiloxan (MD3M)*	*Dodecamethylcyclohexasiloxan (D6)*
Est. Uncertainty	25%	37%	25%	28%	29%	11%

3.2.7 Polycyclic aromatic hydrocarbons

The methods for the determination of polycyclic aromatic hydrocarbons content by gas chromatography coupled to mass spectrometric detection (GC-MS) was fully validated and implemented for the determination of PAHs content in sludge samples.
The method was characterized using Reference Materials such as contaminated soil samples from Intercalibration trials (*i.e.*: contaminated soils S13 and SU6, UNICHIM Interlaboratory Trials "*Polycyclic Aromatic Hydrocarbon in environmental matrices*", 2007 and 2010, respectively). The selectivity, linearity, detection and quantification limits, trueness, repeatability, recovery and stability of the extracts were determined. The uncertainty estimation was based on method performance. This approach is based on the fact that the combined influence of many effects is quantified simultaneously by estimating repeatability, intermediate precision and trueness.

3.2.7.1 Sample preparation

The method was developed for the analysis of the following compounds: Phenantrene, Antracene, Fluoranthene, Pyrene, Benzo(a)antracene, Chrysene, Benzo(b)fluoranthene, Benzo(k)fluoranthene, Benzo(e)pyrene, Benzo(a)pyrene, Perylene, Indeno(1,2,3-cd)pyrene, Dibenz(a,h)antracene, Benzo(g,h,i)perylene, Dibenzo(a,l)pyrene, Dibenzo(a,h)pyrene, Dibenzo(a,i)pyrene, Dibenzo(a,e)pyrene, Coronene.
About 0.1 g of lyophilized compost sample are weighed in a 10 mL glass centrifuge tube and 50 µL of Custom PAH Surrogate Standard Mixture (0.5 ng/µL) are added, followed by approx. 0.5 mL of extraction solvent (Hexane: Acetone, 80:20, %v/v). The mixture is processed by a Vortex for 10 seconds and then submitted to ultrasonic extraction for 30 min. After centrifugation at 1000 rpm for 10 minutes, the supernatant is collected into a clean 10 mL glass centrifuge tube and approx.0.5 mL of extraction solvent (Hexane: Acetone, 80:20, %v/v) is added into the original sample vial. These steps are repeated 4 to 6 times until the sample vial is cleaned. Decantation is done into the same 10mL-glass centrifuge vial where the first extraction solvent was collected. Again Vortex is applied for 10 seconds followed by centrifugation at 1000 rpm for 10 minutes. 50 µL of Custom PAH Syringe Standard Mixture (0.5 ng/µL) added prior to transfer in amber glass vial for analysis.

3.2.7.2 GC-MS analysis

The operating conditions for GC-MS analysis are reported below.

Table 20 - GC MS conditions for PAH analysis

Column	**SGE ID-BPX-50**			
Nominal length	60 m			
Nominal Diameter	250 µm			
Nominal film thickness	0.25 µm			
Mode	constant flow			
Initial flow	1 mL/min			
Oven				
Initial Temperature	100 °C			
Initial Time	3 min			
Ramps:	#	Rate	Final Temp	Final Time
	1	15 °C/min	220 °C	0

	2	2 ℃/min	300 ℃	20
	3	3 ℃/min	340 ℃	30
Run Time 114.33 min				
Front Inlet (CIS4)		**Gerstel CIS 4**		
Mode	Splitless	Initial Temperature	100 ℃	
Initial Temperature	0 ℃	Equilibration Time	0.05 min	
Pressure	144.5 kPa	Initial Time	0.05 min	
Purge Flow	50 mL/min	Rate	12 ℃/sec	
Purge Time	1 min	Final Temp	300 ℃	
Total Flow	53.7 mL/min	Hold Time	3 min	
Gas saver	off			
Gas Type	Helium			
MS Quad	150 ℃			
MS Source	230 ℃			

The analytes were identified using their retention times and selected ion masses. The quantification was made using the response factors between analytes and their isotopically labelled internal surrogate standards. The retention times were detected by analysing periodically the standard solution containing all the compounds and isotopically labelled surrogates and syringe standards.
Linearity of developed procedure in sludge samples was studied for the low concentration range (30 to 500 ng/g) and high concentration range (0 to 9600 ng/g), by analysing 4 calibration solutions for each range. For all compounds at both concentration levels the R^2 values were >0.99. It can be stated, that the analytical method is linear in this range.

3.2.7.3 Performance characteristics

LOD/LOQ

The Limit of Detection (LoD) and the Limit of Quantification (LoQ) were estimated analysing blank samples containing analytes at very low level with signal to noise ratio (RMS S/N) from 8 to 35. The following formulas (recommended by EURACHEM, A Laboratory Guide to Method Validation and Related Topics) were used to calculate the LOD and LOQ values:

$$LOD = blank + 3s_L$$

$$LOQ = blank + 10s_L$$

where the blank is mean value of ten analyses of blank samples and s_L is the standard deviation of these ten replicates.
The LOD and LOQ for the analytes in soil and compost samples are shown in the following Table.

Table 21 LoD and LoQ of PAHs determination by GC-MS

Compound	***LOD ng/g***	***LOQ ng/g***	***Compound***	***LOD ng/g***	***LOQ ng/g***
Phenanthrene	7.2	10.7	Perilene	4.8	7.4
Anthracene	4.6	7.8	Indeno(1,2,3-cd)pyrene	7.9	13.6
Fluoranthene	4.3	5.3	Dibenzo(a,h)anthracene	4.6	7.9
Pyrene	4.8	6.0	Benzo(g,h,i)perilene	6.6	11.6

Compound	*LOD ng/g*	*LOQ ng/g*	*Compound*	*LOD ng/g*	*LOQ ng/g*
Benzo(a)anthracene	4.0	5.6	Dibenzo(a,l)pyrene	58.7	92.9
Chrysene	4.7	6.8	Dibenzo(a,h)pyrene	56.4	97.0
Benzo(b)fluoranthene	7.6	10.7	Dibenzo(a,i)pyrene	585.9	848.0
Benzo(k)fluoranthene	6.5	11.6	Dibenzo(a,e)pyrene	664.1	961.9
Benzo(e)pyrene	7.4	11.5	Coronene	53.6	88.1
Benzo(a)pyrene	4.3	6.4			

Recovery

Recovery values were evaluated by the ratio between each surrogate compound and the opportune labelled compound added to sample extracts as syringe standard. Recovery was calculated in two different concentration levels using the data received on the repeatability and intermediate precision study. The average recovery results are shown in the following Table.

Table 22 Recoveries of PAHs

Compound	*S13, high C*	*SU6, low C*	*Compound*	*S13, high C*	*SU6, low C*
Phenantrene	62%	76%	Perylene	69%	71%
Antracene	64%	78%	Indeno(1,2,3-cd)pyrene	67%	59%
Fluoranthene	67%	89%	Dibenz(a,h)antracene	74%	69%
Pyrene	68%	83%	Benzo(g,h,i)perylene	56%	51%
Benzo(a)antracene	74%	80%	Dibenzo(a,l)pyrene	63%	33%
Chrysene	74%	80%	Dibenzo(a,h)pyrene	63%	33%
Benzo(b)fluoranthene	75%	72%	Dibenzo(a,i)pyrene	63%	33%
Benzo(k)fluoranthene	75%	72%	Dibenzo(a,e)pyrene	63%	33%
Benzo(e)pyrene	70%	70%	Coronene	31%	30%
Benzo(a)pyrene	76%	70%			

Uncertainty

Expanded uncertainty (U) was estimated using the approach, where the repeatability, intermediate precision and trueness estimation results were combined, using the following formula:

$$U = k\sqrt{{u_r}^2 + {u_{ip}}^2 + u_t^2};$$

where,

$$u_r = \frac{s_r}{\sqrt{n}},$$

where $\mathbf{s_r}$ is the relative repeatability standard deviation from the validation study and **n** is the number of replicates performed;

$$u_{ip} = \frac{s_d}{\sqrt{d}},$$

where $\mathbf{s_d}$ is the relative day-to-day variation from the validation study and **d** is the number of days over which the measurements were spread;

$$u_t = \sqrt{\frac{s_t^2}{n_t} + \frac{\sum u_{mat}^2}{n_{mat}^2}},$$

where $\mathbf{s_t}$ and $\mathbf{n_t}$ are accordingly the relative standard deviation and the number of replicates of the trueness experiment of the validation study and $\mathbf{u_{mat}}$ and $\mathbf{n_{mat}}$ are accordingly the relative uncertainty and the number of materials used for trueness estimation. As the certified soil samples from Intercalibration trials were used as CRM, the u_{mat} was calculated as follows:

$$u_{mat} = \frac{s_i}{\sqrt{n_i}},$$

where $\mathbf{s_i}$ is the standard deviation of the results in intercalibration trials and $\mathbf{n_i}$ is the number of laboratories participated in this trial;

k is the coverage factor, a coverage factor of 2 is chosen to give about 95% probability.
The relative influences of repeatability, intermediate precision and trueness (bias) are shown in the Table 21. Because of the time factor and lack of the CRMs It was not possible to estimate the uncertainty for each compound.

Table 23 Repeatability, intermediate precision and trueness of PAHs determination

Compound	***HIGH conc.***			***LOW conc.***		
	u(r)	**u(ip)**	**u(t)**	**u(r)**	**u(ip)**	**u(t)**
Phenanthrene	0.3%	4.3%	10%	0.2%	4.8%	
Anthracene	0.9%	3.0%	10%	4.2%	5.5%	12%
Fluoranthene	0.7%	4.1%	10%	0.7%	4.1%	11%
Pyrene	0.5%	3.2%	10%	0.5%	4.3%	10%
Benzo(a)anthracene	0.2%	2.8%	10%	0.5%	5.8%	10%
Chrysene	0.3%	2.2%	10%	0.3%	5.6%	10%
Benzo(b)fluoranthene	0.3%	2.0%	10%	0.4%	4.7%	10%
Benzo(k)fluoranthene	0.3%	1.7%	10%	1.4%	5.3%	10%
Benzo(e)pyrene	0.3%	1.6%		0.2%	4.4%	10%
Benzo(a)pyrene	0.5%	1.3%	10%	0.6%	6.4%	11%
Perilene	1.1%	2.0%		1.2%	5.7%	
Indeno(1,2,3-cd)pyrene	0.9%	2.9%		1.4%	6.3%	12%
Dibenzo(a,h)anthracene	0.9%	2.2%	11%	2.3%	4.5%	
Benzo(g,h,i)perilene	0.7%	2.3%	11%	0.5%	5.4%	10%
Dibenzo(a,l)pyrene						
Dibenzo(a,h)pyrene				1.3%	8.3%	
Dibenzo(a,i)pyrene						
Dibenzo(a,e)pyrene						
Coronene	2.1%	5.8%		0.6%	8.1%	

Taking into account that the estimated combined uncertainties for analytes did not vary a lot (relative standard deviation is less than 10%) and there were no available data that could be used for uncertainty evaluation for each analyte the mean combined uncertainty must be applied for each compound. The mean uncertainty was calculated from expanded uncertainties for low concentration level, as they are bigger than the same figures calculated for high concentration level.
The expanded relative uncertainty that applies for all analytes was calculated to be 24%.
The estimated combined uncertainties together with expanded uncertainties are shown in the following Table.

Table 24 Combined uncertainties and expanded uncertainties for PAHs

Compound	***high conc.***		***low conc.***	
	u	**U**	**u**	**U**
Phenanthrene	11%	**22%**		
Anthracene	11%	**21%**	14%	**28%**
Fluoranthene	11%	**22%**	12%	**23%**
Pyrene	10%	**21%**	11%	**22%**
Benzo(a)anthracene	11%	**21%**	12%	**24%**
Chrysene	11%	**21%**	12%	**24%**
Benzo(b)fluoranthene	10%	**20%**	11%	**22%**
Benzo(k)fluoranthene	10%	**20%**	12%	**24%**
Benzo(e)pyrene			11%	**22%**
Benzo(a)pyrene	10%	**20%**	12%	**25%**
Indeno(1,2,3-cd)pyrene			13%	**27%**
Dibenz(a,h)anthracene	12%	**23%**		
Benzo(g,h,i)perilene	11%	**22%**	11%	**23%**
AVERAGE		**21%**		**24%**
Rel. St. Deviation		**5%**		**8%**

3.2.8 Perfluoroalkyl substances

Two perfluoroalkyl carboxylates (PFOA (C8) and PFNA (C9)) and perfluorooctane sulfonate (PFOS) were analysed by ultra-high pressure liquid chromatography coupled to tandem mass spectrometric detection (UHPLC-MS-MS). Internal quantification was applied for PFAS determination by the use of labeled surrogate analogues (PFOA $^{13}C_4$, PFNA $^{13}C_5$, and PFOS $^{13}C_4$).

The PFASs were extracted from the sludge samples by solid-liquid extraction (SLE) with methanol in an ultrasonic bath followed by Envi-Carb graphitised carbon clean-up. This "matrix effect-free" extraction method for the determination of various PFASs in soil, sediment and sludge with LOQs in the ng/g range was described by Powley et al. (2005) [**96**]. The analytical protocol is straightforward and robust; Due to its simple handling and reliable results, this method became the basis for many applications thereafter (Jahnke and Berger, 2009) [**97**].

The method was validated using a sewage sludge reference material from a previous intercalibration study ("Interlaboratory study on perfluorinated compounds in environmental and human matrices"). The JRC participated in this international interlaboratory study on PFASs in environmental matrices (water, fish, and sludge) (Van Leeuwen et al., 2011) [**98**]. The sludge sample was provided by WEPAL (www.wepal.nl) and originated from the Netherlands. The bulk sludge material was dried at 40°C, milled to pass a 0.5 mm sieve, homogenized and filled into individual bottles. The extraction efficiency, detection and quantification limits were determined.

3.2.8.1 Sample preparation

A about 1 gr. of lyophilized sludge sample is weighed in a 50 mL Sarstedt PP conical centrifuge tube and 100 µL of internal standard solution (PFOA $^{13}C_4$, PFOS $^{13}C_4$ and PFNA $^{13}C_5$, 1 mg/L in methanol) are added with 10 mL of pure methanol. After Vortex-application for 30 seconds and ultrasonic extraction for 18 minutes, the samples are centrifuged at 1000 rcf for 10 minutes. 1 mL of supernatant are transferred into a 1.5 mL disposable polypropylene micro centrifuge tubes containing 25 mg of ENVI-Carb sorbent previously

acidified with 50 µL of glacial acetic acid. Upon Vortex for 30 seconds and centrifugation at 6720 rcf for 30 minutes, 0.8 µL of supernatant are transferred into adequate tubes for concentration to 200 µL under gentle stream of nitrogen at 35C. 200 µL of water are added followed by homogenization with Vortex. The ready solution is the transferred to LC-MS/MS vials for analysis.

3.2.8.2 Performance characteristics

Extraction efficiency

Extraction efficiency was evaluated by subsequent extraction of selected sewage sludge samples, according to the procedure reported above. The results of extraction efficiency, also summarised in the following table, were: 66.7 ± 4.9% for PFOA, 66.0 ± 13.9% for PFNA and 87.1 ± 12.5% for PFOS.

Table 25 Extraction efficiency for PFASs (n=4)

PFOA	**2nd extraction**	**1st extraction**		
	Conc (ng/g)	**Conc (ng/g)**	**Total conc (ng/g)**	**Extraction Efficiency**
	1.104	1.720	2.824	60.9
	1.251	2.492	3.743	66.6
	3.623	9.712	13.336	72.8
	1.046	2.075	3.120	66.5
			Average	**66.7**
			St. Dev.	**4.87**
			CV%	**7.3**
PFNA	**2nd extraction**	**1st extraction**		
	Conc (ng/g)	**Conc (ng/g)**	**Total conc (ng/g)**	**Extraction Efficiency**
	1.345	2.154	3.499	61.6
	1.247	3.182	4.429	71.8
	1.061	4.651	5.712	81.4
	1.559	1.502	3.061	49.1
			Average	66.0
			St. Dev.	13.88
			CV%	21.0
PFOS	**2nd extraction**	**1st extraction**		
	Conc (ng/g)	**Conc (ng/g)**	**Total conc (ng/g)**	**Extraction Efficiency**
	1.269	10.403	11.672	89.1
	3.870	61.407	65.277	94.1
	3.703	8.244	11.947	69.0
	1.115	29.825	30.940	96.4
			Average	87.1
			St. Dev.	12.47
			CV%	14.3

Limit-of-Detection (LoD)

The compound-dependent method detection limits (MDLs or LODs) for the procedure were calculated from the mean concentrations of procedural blanks plus 3 times the standard deviation. 0.1 g of freeze-dried sewage sludge was extracted with 10 mL of solvent, of which one mL was subjected to graphitised carbon black clean-up and concentrated to 0.2 mL, which results in an enrichment factor of 40. The LOD for the analytes in samples are shown in the following Table.

Table 26 LoD of PFASs determination by UHPLC-MS/MS

Conc (ng/g)		
PFOA	**PFNA**	**PFOS**
0.200	0.300	0.500

Uncertainty

Measurement uncertainties of analytical methods can be calculated by the analysis of certified reference materials (CRMs), or from the z-scores derived from interlaboratory studies. The JRC-IES laboratory participated in, the 3rd international interlaboratory study on PFASs [94] and used the material therein characterised for method development.

In this interlaboratory study, for the first time, a sewage sludge sample was included. The variance for the results in this matrix was substantial, showing that more effort is needed to improve methods for sludge.

The assigned values of the interlaboratory study were: 10.7 ng/g for PFOA, 0.39 ng/g for PFNA, and 89.3 ng/g for PFOS. The RSDs between the laboratories were relatively high: 58 % for PFOA (n=25), 139 % for PFNA (n=12), and 47 % for PFOS (n=27).

The JRC results were (laboratory 16): 16.5 ng/g for PFOA (z-score: 4.3), 4.5 ng/g for PFNA (z-score: 67.1), and 62.0 ng/g for PFOS (z-score: -2.5). Note that the concentration for PFNA was very low; therefore the variation was high.

This comparison shows a relative good agreement for PFOS and PFOA with acceptable uncertainties of the JRC-IES laboratory. The sewage sludge samples of Fate Sees, however, were analysed by UHPLC-MS-MS, with higher sensitivity.

3.2.9 Semi-quantitative non-target screening

A multi-residue analytical method, based on ultra-high performance liquid chromatography-tandem mass spectrometry (UHPLC-MS/MS), was applied in the analysis of sewage sludge samples for the detection and semi-quantitative determination of more than 60 multiple-class compounds, including pesticides, phenols, sweeteners, pharmaceuticals, benzotriazoles and personal care products.

Semi-quantitative determination was performed using external standard quantification method comparing the area counts of the compound's MRM transitions in the sample and the corresponding MRM transition in the analytical standard. The studied compounds and their respective MRM transitions are listed in the table below.

Table 27 Selected organic contaminants and relative MRM transitions

Compound	***MRM transitions***	***Compound***	***MRM transitions***
Atrazine	216 > 174; 104	2,4-D	219 > 161; 125
Atrazine-desethyl	188 > 146; 104	2,4,5-T	255 > 197; 161

Compound	*MRM transitions*	*Compound*	*MRM transitions*
Atrazine-desisopropyl	174 > 104; 79	Mecoprop	213 > 141; 105
Terbutylazine	230 > 174; 132	Bentazone	239 > 132; 197
Terbutylazine-desethyl	203 > 78	MCPA	199 > 141; 105
Terbutryn	242 > 186; 91	Dichlorprop	233 > 161; 125
Simazine	202 > 104; 132	Nitrophenol	138 > 108; 92
Propazine	230 > 146; 188	2,4-Dinitrophenol	183 > 109; 123
Diuron	233 > 72; 133	Acesulfame K	162 > 78; 82
Isoproturon	207 > 72; 165	Sucralose	395 > 359
Chlortoluron	336 > 235; 219	Saccharin	182 > 42; 106
Linuron	249 > 160; 133	Acetylsalicylic acid	137 > 93
Alachlor	270 > 238; 162	Carbamazepine	237 > 194; 165
Metolachlor	284 > 252; 176	Ibuprofen	205 > 161; 159
Diazinon	305 > 169; 97	Diclofenac	294 > 250; 214
Molinate	188 > 126; 98	Ketoprofen	253 > 209; 197
Metoxuron	229 > 72; 156	Naproxen	229 > 169; 185
Hexazinone	253 > 171; 85	Gemfibrozil	249 > 121; 106
Carbaryl	202 > 145; 127	Clofibric acid	213 > 127; 85
Carbendazim	192 > 160; 105	Bezafibrate	360 > 274; 154
Carbofuran	222 > 123; 165	Atenolol	267 > 145; 190
Chloridazon	222 > 77; 65	Metopropol	268 > 116; 103
Chloridazon-desphenyl	213 > 72; 140	Propanolol	260 > 255; 237
Chloridazon-methyl-desphenyl	60 > 88; 101	Sotalol	273 > 133; 255
Fenitrothion	278 > 109; 79	Tamoxifen	372 > 72; 129
Flusilazole	316 > 165; 247	Triclosan	287 > 35
Iprodion	331 > 246	Caffeine	195 > 138; 110
Ioxynil	370 > 127; 215	DEET	192 > 91; 119
Imidacloprid	254 > 153; 86	1H-Benzotriazole	120 > 65; 92
Methabenzthiazuron	222 > 165; 150	1-Methyl-benzotriazole	134 > 77; 106
Tolylfluanid	347 > 137; 238	Benzothiazole	136 > 109; 65
Vinclozolin	316 > 284; 75		

3.2.9.1 Sample preparation

About 1 gr. of lyophilized sludge sample is weighed in a 50 mL Sarstedt PP conical centrifuge tube and 100 µL of internal standard solution (PFOA $^{13}C_4$, PFOS $^{13}C_4$ and PFNA $^{13}C_5$, 1 mg/L in methanol) followed by 10 mL of pure methanol are added. After Vortex for 30 seconds and ultrasonic extraction for 18 minutes, the samples is centrifuged at 1000 rcf for 10 minutes and 1 mL of supernatant are transferred into 1.5 mL disposable polypropylene micro centrifuge tubes containing 25 mg of ENVI-Carb sorbent previously acidified with 50 µL of glacial acetic acid. After Vortex for 30 seconds and centrifugation at 6720 rcf for 30 minutes 0.8 µL of supernatant are transferred into adequate tubes for concentration to 200 µL under gentle stream of nitrogen at 35°C. 200 µL of water are added and the solution is mixed with Vortex before transfer into a LC-MS/MS vial for analysis.

3.2.9.2 Rational of semi-quantitative screening approach and criteria followed for quantification analysis and

The rationale behind the semi-quantitative determination of polar compounds is based on the capability of Envicarb to adsorb compounds via dispersive interaction with π electrons. In case of chemicals containing no π electrons, there is no possibility for specific π – π interactions between the sorbent and analytes of interest. The purification of sludge is due to the association of organic compounds showing any degree of aromaticity (π electrons). More aromatic compounds exibit, obviously, a stronger association to Envi-carb, resulting in a loss of concentration in methanolic solution treated with the sorbent.
Our experimental data demonstrate that putting a methanolic solution containing the selected polar compounds in contact with acidified Envi-Carb and following the developed procedures for sewage sludge sample, in most of cases does not affect so much the response of analytes in methanolic solution and the subsequent calculated concentration.

Table 28 Recovery values (n=3) of polar compounds from Envicarb

Analyte Peak Name	Rec %	Analyte Peak Name	Rec %
2,4-D	44.1	1-Methyl-1H-benzotriazole	60.1
2,4-D1	35.7	1-Methyl-1H-benzotriazole1	57.1
2,4-Dinitrophenol	29.4	1-Methyl-1H-benzotriazole2	59.6
2,4-Dinitrophenol1	29.7	1H-Benzotriazole	65.0
2,4,5-T	12.9	1H-Benzotriazole1	73.4
2,4,5-T1	12.1	Caffeine	30.8
Acesulfame K	63.0	Caffeine1	37.4
Acesulfame K1	65.1	Carbamazepine	75.7
Acetylsalicylic acid	51.6	Carbamazepine1	67.5
Bentazone	63.5	Clarithromycin	98.4
Bezafibrate	4.5	Clarithromycin1	107.1
Bezafibrate1	3.9	Diuron	29.6
Chloramphenicol	77.2	Diuron1	30.3
Chloramphenicol1	76.2	Roxithromycin	77.0
Clofibric acid	47.8	Roxithromycin1	79.0
Clofibric acid1	52.3	Trimethoprim	100.0
Dichlorprop	32.0	Trimethoprim1	102.8
Dichlorprop1	32.3		
Diclofenac	1.5		
Diclofenac1	1.7		
Gemfibrozil	2.8		
Gemfibrozil1	2.5		
Ibuprofen	9.4		
Ibuprofen1	12.2		
Imidacloprid	61.6		
Imidacloprid1	63.5		
Ketoprofen	14.5		
Ketoprofen1	12.9		

Analyte Peak Name	Rec %	Analyte Peak Name	Rec %
MCPA	34.7		
MCPA1	35.2		
Mecoprop	26.2		
Mecoprop1	21.6		
Naproxen	10.8		
Naproxen1	15.7		
Nitrophenol	61.9		
Nitrophenol1	66.9		
Saccharin	57.7		
Saccharin1	59.4		
Sucralose	67.1		

For most of the compounds, the reported concentration was underestimated at maximum of 2-5 times (so in the same order of magnitude), error that could be considered acceptable for a semi-quantitative screening method (as it was our aim).
Special attention could be devoted to bezafibrate, diclofenac and gemfibrozil. For these analytes the exact concentrations is probably ten folds higher than reported.

The criteria followed for analytes semi-quantitativw determination are the following:
two MRM transitions between the precursor ions and two most abundant fragment ions were monitored for almost every compound. The first one was used for quantification purposes, whereas the second one was to confirm the presence of the target compounds in the sample. In this way, the number of identification points (IPs) needed to confirm the detection of target analytes, according to the EU Regulations (4 IP, 1 for precursor ion and 1.5 for each transition product, EU Commission Decision 2002/657/EC) was reached. Besides the monitoring of MRM transitions, other identification criteria were used for quantification:

- LC retention time of the compound in the standard compared to those obtained in the samples. Retention time in the sample must be within ± 2% the retention time of the analyte in the analytical standard.
- The relative abundance of the two selected MRM transitions in the sample must be within ± 20% of the ratio obtained in the analytical standard.

Results and discussions of FATE-SEES

A total of 61 sewage sludge samples were collected in 15 European countries. Number of samples collected in each country is summarised in the table below. The map of collected sewage sludge samples as well as some further information on related samples taken at the same occasion is illustrated in Figure 1.

Table 29 Number of sludge samples collected in each country.

Country	***N. samples***	***Country***	***N. samples***
Austria	2	Lithuania	3
Belgium	9	Portugal	2

Czech Republic	2	Romania	1
Finland	6	Slovenia	1
Germany	6	Sweden	8
Greece	3	Switzerland	9
Hungary	1	The Netherlands	6
Ireland	2		

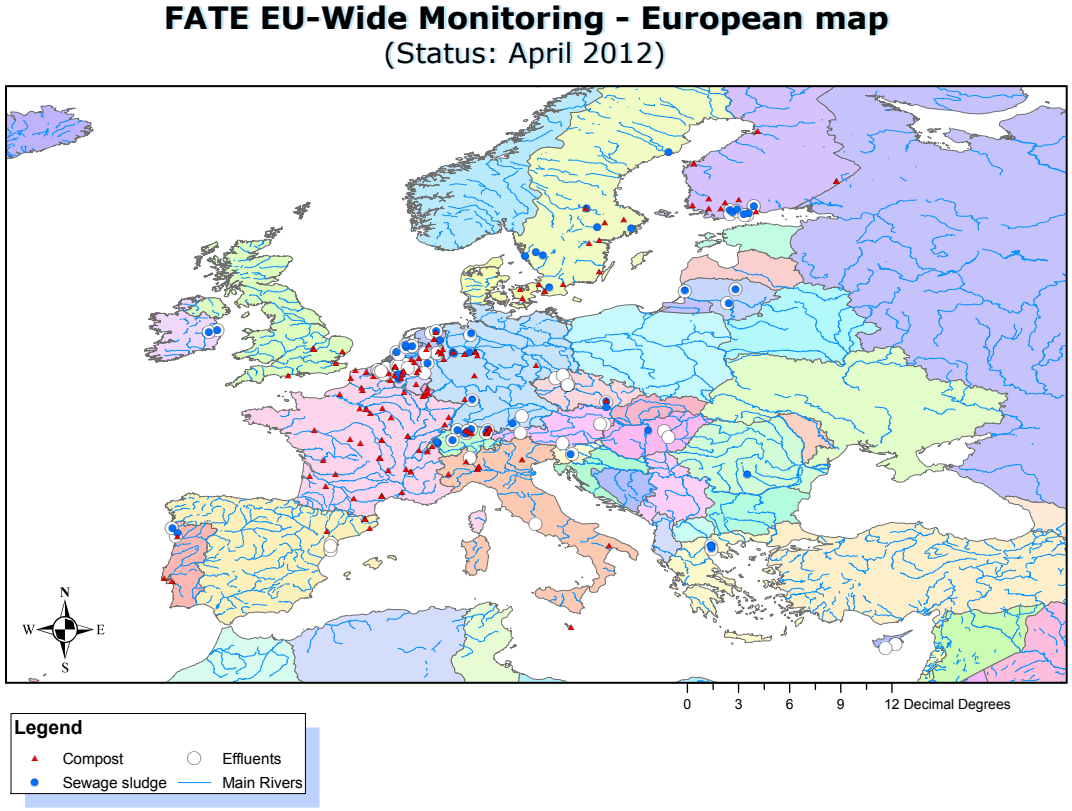


Figure 1 - Map of sampling sites accessed during FATE-SEES and the related exercise on biowastes FATE-COMES (approximate locations)

An analogous campaign was carried out by U.S. Environmental Protection Agency (U.S. EPA) between 2006 and 2007. Within the Target National Sewage Sludge Survey (TNSSS), 84 treated sewage sludge samples were collected in 74 publicly owned WWTPs located in the Unites States [3]. All samples were analysed for 145 pollutants, including both organic and inorganic compounds. The main differences between the two projects reside in the type of WWTPs considered. In the U.S. EPA survey, only municipal WWTP were considered, while in the FATE-SEES campaign both industrial and municipal facilities were examined. Moreover, statistics were made on a different number of samples: 84 in United States and 61 in Europe. In the computation of statistic parameters, when no uncensored data were available for <LOQ and not detectable concentrations (n.d.), they were replaced with the most used estimate, DL/2. However, when more than 50% of data in the analyzed chemicals is <LOQ (or n.d.) only minimum and maximum values were listed in tables.

3.3.1 Descriptive statistics

3.3.1.1 Metals

Uncensored data (ICP/AES true values) were used for statistical analysis when values were below LoD. However, when negative data occurred, they were replaced with the LoD/2 estimate.
In tables, the regulation limit values for heavy metals concentration in sludge for their use in agriculture, defined in the *Directive 86/278/EEC*, were listed together with the number of exceeding values for the analysed metals.

Table 30 Descriptive statistic for analyzed metals in sludge samples.
Number of samples: 61

	Ag	***As***	***Ba***	***Cd***	***Co***	***Cr***	***Cu***
U.o.m.	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*
Min	<DL	<DL	41,5	<DL	1,5	10,8	27,3
Max	14,7	56,1	580	5,1	16,7	1542	578
Average	3,3	-	225	0,9	6,3	79,8	257
STD	3,0	-	102	0,7	3,3	215	118
Median	2,4	-	197	0,9	5,6	37,9	240
90% percentile	8,0	-	350	1,3	11,1	80,5	418
CV (%)	91	-	45	75	53	269	46
BDL (%)	5	66	0	7	0	0	0
MV (%)	0	0	0	0	0	0	0
Positive detection (%)	95	34	100	93	100	100	100
86/278/EEC limit	-	-	-	20-40	-	-	1000-1750
Exceeding	-	-	-	0	-	-	0

	Hg	***Mn***	***Mo***	***Ni***	***Pb***	***Sb***	***Ti***
U.o.m.	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*
Min	0,1	75,2	1,7	8,6	4,0	<DL	65,2
Max	1,1	960	12,5	310	430	53,6	1071
Average	0,4	329	4,9	29,0	47,6	6,0	440
STD	0,2	193	1,9	40,2	59,3	8,2	255
Median	0,4	281	5,0	20,1	30,4	3,9	350
90% percentile	0,7	604	7,1	34,9	81,2	9,1	764
CV (%)	52	59	38	139	125	137	58
BDL (%)	0	0	0	0	0	34	0
MV (%)	0	0	0	0	0	0	0
Positive detection (%)	100	100	100	100	100	66	100
86/278/EEC limit	16-25	-	-	300-400	750-1200	-	-

	V	***Al***	***Fe***	***K***	***Mg***	***P***	***Zn***
U.o.m.	*mg/kg*	*%*	*%*	*%*	*%*	*%*	*%*
Min	2,3	0,1	0,2	0,10	0,01	1,0	0,02
Max	135	6,0	14,9	2,6	2,24	5,6	0,12
Average	25,0	1,7	3,8	0,43	0,44	3,1	0,07
STD	20,3	1,2	3,6	0,39	0,33	1,1	0,02
Median	21,5	1,3	2,5	0,33	0,37	2,9	0,07

90% percentile	39,8	3,1	8,5	0,74	0,80	4,8	0,09
CV (%)	81	71	94	90	76	36	35
BDL (%)	0	0	0	0	0	0	0
MV (%)	0	0	0	11	0	11	0
Positive detection (%)	100	100	100	89	100	89	100
86/278/EEC limit	-	-	-	-	-	-	0,25-0,40
Exceeding	-	-	-	-	-	-	0

In the following graphs, average, median and 90° percentile were shown for analyzed metals in sewage sludge samples.

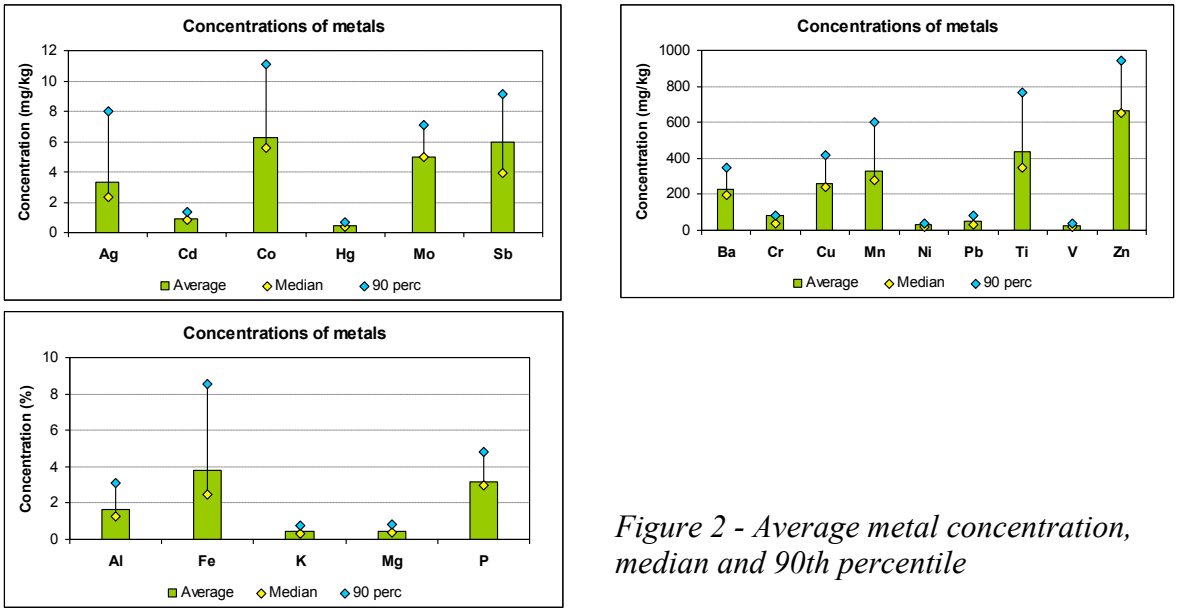
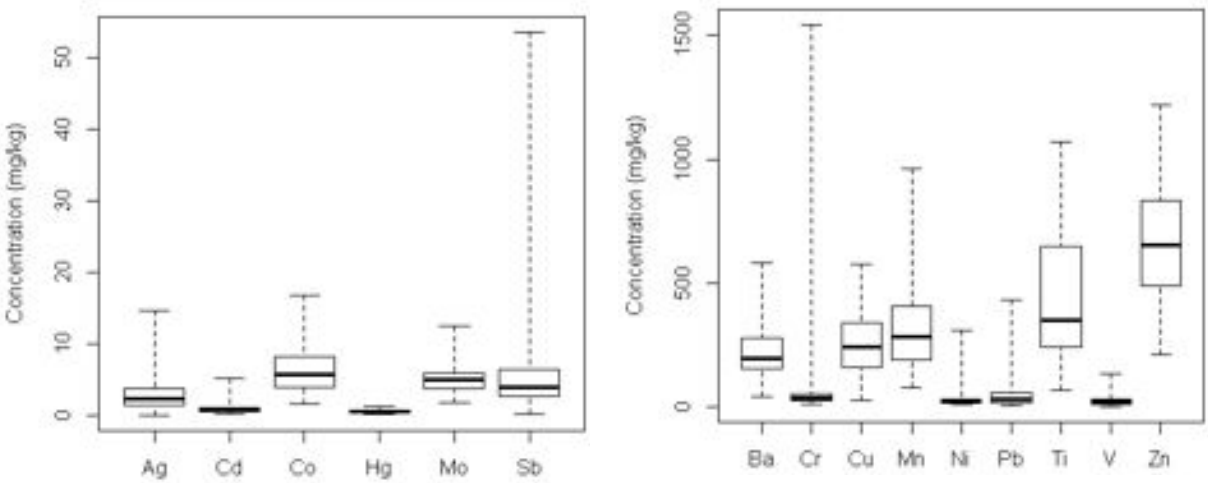


Figure 2 - Average metal concentration, median and 90th percentile

The high coefficient of variation found for the majority of the measured elements was expected, because samples came from different WWTPs located in several European countries. In particular, from the following boxplots it can be shown that elements with greatest variation are Sb, Cr and Fe. In boxplots, the minimum, 1st quartile (25th percentile), 3rd quartile (75th percentile), median, and maximum are shown.



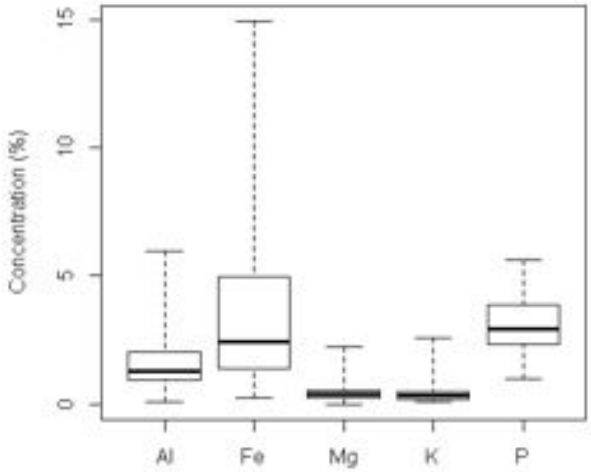


Figure 3 - Boxplots of analysed metals concentrations

3.3.1.2 PAHs

When observed values where below the LoD, LoD/2 was used as an estimate for statistical analysis.

Table 31 Descriptive statistic for analyzed PAHs in sludge samples.
Number of samples: 32

	Phenantrene	***Antracene***	***Fluoranthene***	***Pyrene***	***Benzo(a) antracene***	***Chrysene***	***Benzo(b) fluoranthene***
U.o.m.	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*
Min	29,9	<DL	34,5	47,2	<DL	<DL	<DL
Max	5552	724	3217	2637	1833	2021	1919
Average	644	95,5	814	698	438	504	601
STD	1084	138	825	643	443	483	503
Median	265	51,6	499	502	306	325	595
90% percentile	977	191	2080	1558	982	1076	1351
CV (%)	168	144	101	92	101	96	84
BDL (%)	0	16	0	0	3	6	9
Positive detection (%)	100	84	100	100	97	94	91

	Benzo(k) fluoranthene	***Benzo(e) pyrene***	***Benzo(a) pyrene***	***Perylene***	***Indeno(1,2,3-cd) pyrene***	***Dibenz(a,h) antracene***
U.o.m.	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*
Min	9,9	18,9	17,9	<DL	24,2	<DL
Max	1048	1477	1476	544	1401	548
Average	260	339	370	115	342	134
STD	247	352	370	146	354	138
Median	177	261	255	49,4	241	91,1
90% percentile	636	736	869	277	764	311

CV (%)	95	104	100	127	103	103
BDL (%)	0	0	0	41	0	3
Positive detection (%)	100	100	100	59	100	97

	Benzo(g,h,i) perylene	***Dibenzo(a,l) pyrene***	***Dibenzo(a,h) pyrene***	***Dibenzo(a,i) pyrene***	***Dibenzo(a,e) pyrene***	***Coronene***
U.o.m.	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*
Min	29,7	<DL	<DL	-	<DL	<DL
Max	1335	60	433	-	73,4	550
Average	356	-	111	-	-	170
STD	333	-	111	-	-	145
Median	276	-	59,6	-	-	142
90% percentile	729	-	258	-	-	362
CV (%)	94	-	100	-	-	85
BDL (%)	0	91	31	100	94	16
Positive detection (%)	100	9	69	0	6	84

In the following graphs, average, median and 90° percentile are shown for analysed PAHs in sewage sludge samples.

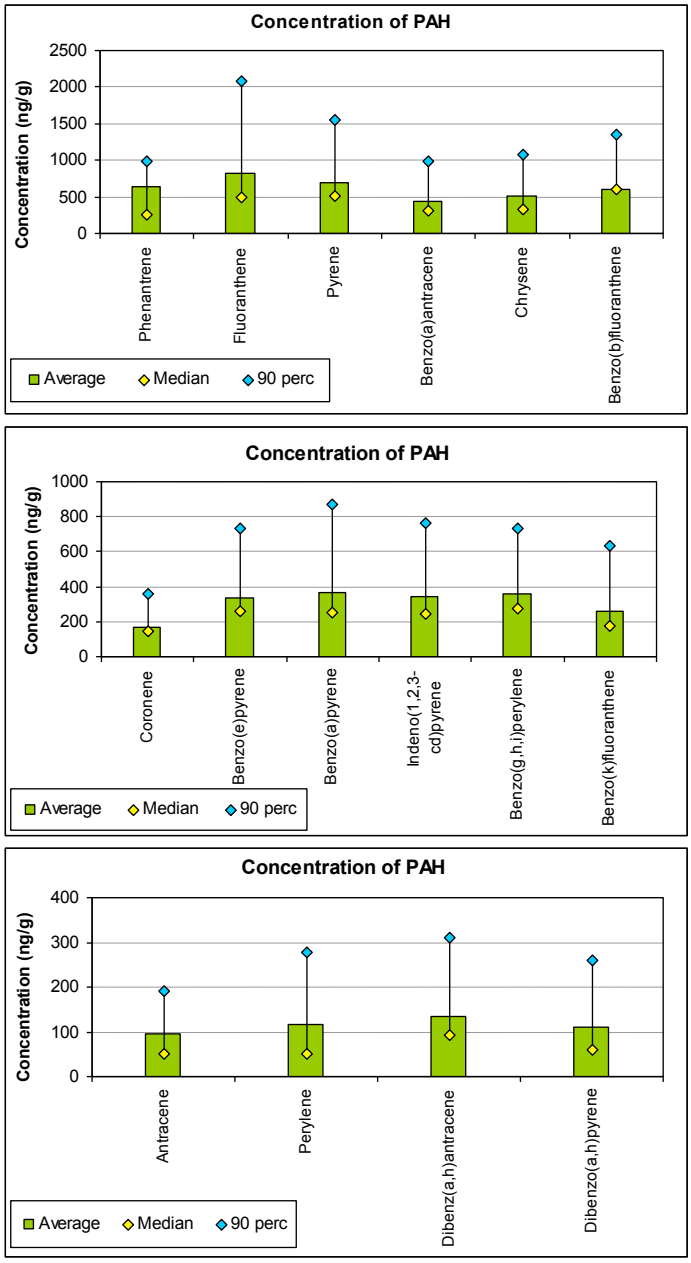


Figure 4 - Average PAHs concentration, median and 90°percentile

The high coefficient of variation found for the majority of the measured PAHs was expected, because samples came from different WWTPs located in several European countries. In the following boxplots, the minimum, 1st quartile (25th percentile), 3rd quartile (75th percentile), median, and maximum are shown.

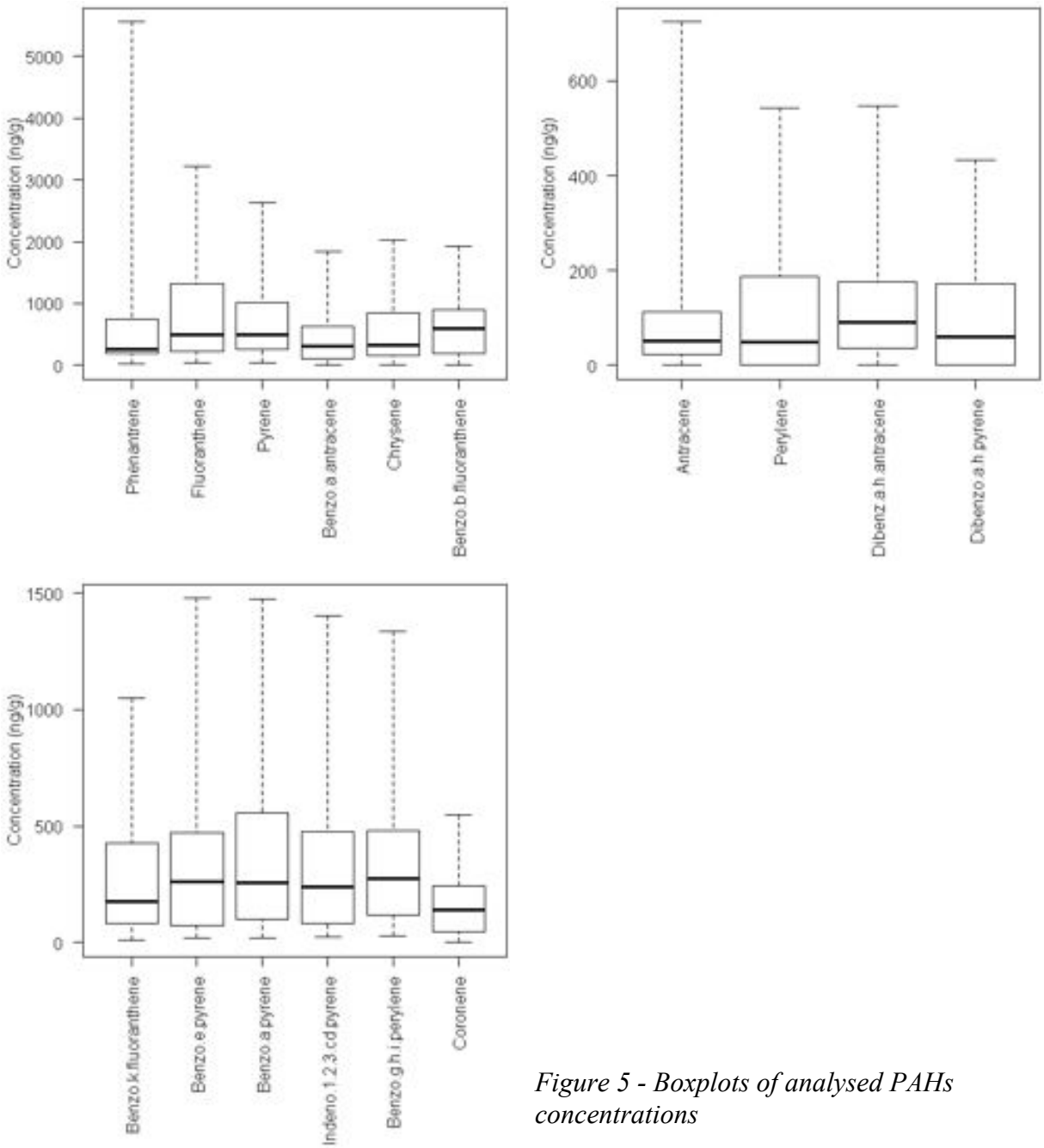


Figure 5 - Boxplots of analysed PAHs concentrations

3.3.1.3 PCM

When observed values where below the LoD, LoD/2 was used as an estimate for statistical analysis.

Table 32 Descriptive statistic for analyzed PCM in sludge samples.
Number of samples: 56

	Cashmeran	***Celestolid***	***Phantolid***	***Traesolid***	***Galaxolid***	***Tonalid***
U.o.m.	*µg/kg*	*µg/kg*	*µg/kg*	*µg/kg*	*µg/kg*	*µg/kg*
Min	<DL	<DL	<DL	<DL	1100	210
Max	560	120	65	1300	51000	4000
Average	90	38	-	200	10802	1026
STD	102	27	-	255	8372	733
Median	60	33	-	135	8600	890
90% percentile	185	82	-	345	17500	1800
CV (%)	113	71	-	127	78	71
BDL (%)	13	14	52	2	0	0
Positive detection (%)	88	86	48	98	100	100

In the following graphs, average, median and 90° percentile were shown for analysed PCM in sewage sludge samples.

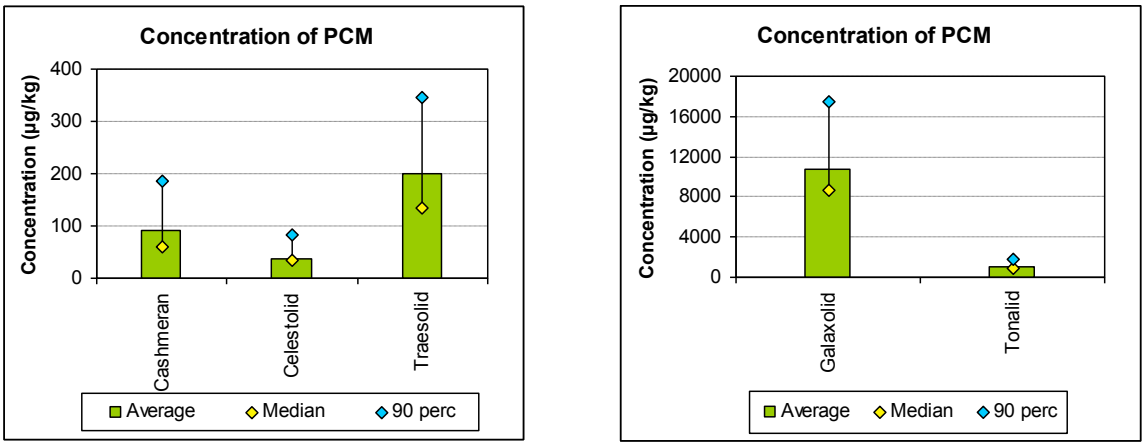


Figure 6 - Average PCM concentration, median and 90°percentile

The high coefficient of variation found for the measured PCM was expected, because samples came from different WWTPs located in several European countries. In the following boxplots, the minimum, 1st quartile (25th percentile), 3rd quartile (75th percentile), median, and maximum are shown.

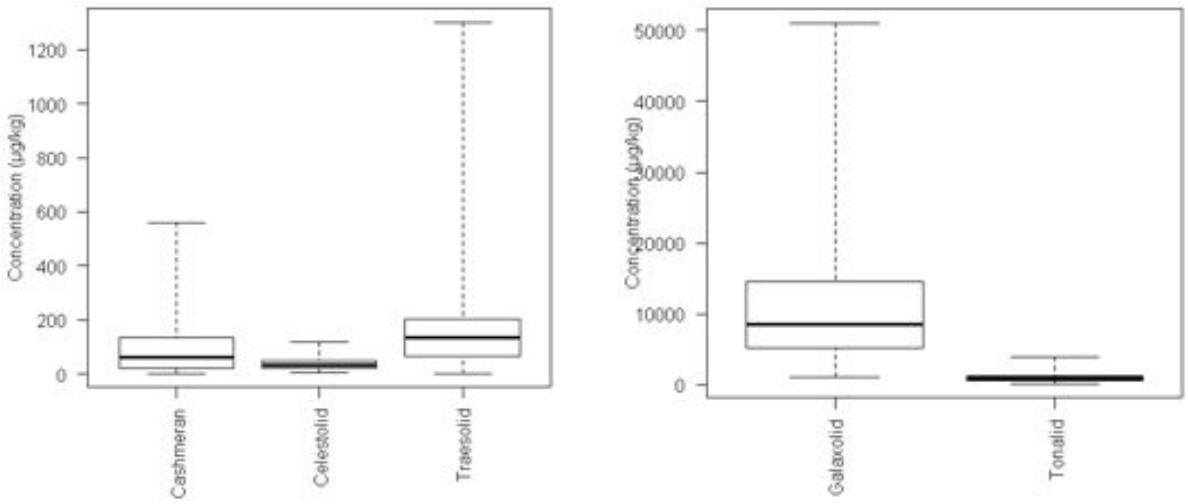


Figure 7 - Boxplots of analysed PCM concentrations

3.3.1.4 PFASs

Polyfluorinated compounds (PFCs) are useful anthropogenic chemicals that have been incorporated into a wide range of products for the past six decades. This class of compounds includes thousands of chemicals, but is best known for the perfluorosulfonates (PFSAs) such as perfluorooctane sulfonate (PFOS), and the perfluorocarboxylic acids (PFCAs) which include perfluorooctanoic acid (PFOA). Concerns about these compounds have developed as many satisfy the defining characteristics of persistent organic pollutants (POPs): they are toxic, extremely resistant to degradation, bioaccumulate in food chains, and can have long half-lives in humans. They are ubiquitous present in the environment and wildlife, and further have been found in human blood serum worldwide (Lindstrom et al., 2011a,b) [**99**].

PFOA and PFOS are relatively well soluble in water (680 mg/L at 24-25°C for PFOS; OECD, 2002) [**100**], but do adsorb as well to suspended particulate matter (SPM), sediment and sludge; PFOS better than PFOA (Zhou et al., 2010) [**101**]. Several publications have already reported the occurrence of different PFASs in sewage sludge around the world (see Table below). WWTPs serve as point sources of PFASs both for the aquatic ecosystems and the terrestrial environment through application of sewage sludge on soil and agricultural fields. Although controversial, the application of sewage sludge as fertilizer to agricultural land is widely used in several countries. Application of sewage sludge to soil may therefore be a potential route for PFASs to enter the terrestrial environment. Recent studies have demonstrated that the application of PFASs contaminated biosolids (*i.e.*: sewage sludge) can have important effects on local environments, ultimately leading to demonstrable human exposures (Lindstrom et al., 2011b; Sepulvado et al., 2011) [**102**]. E.g., in Decatur, Alabama, USA, high PFASs levels in soil samples (PFOA up to 320 ng/g; PFOS up to 410 ng/g) from PFASs contaminated sludge applied fields were found (Washington et al., 2010) [**103**]. There was also a serious PFASs contamination case in Germany (Sauerland case) (Hölzer et al., 2011 [**104**]

In the effluents of WWTPs usually higher PFOA and PFOS concentrations are found than in the influents, due to the formation of these chemicals from precursor substances such as fluorotelomer alcohols (FTOH), fluoroalkyl-sulfonamides, or other PFCs (Becker et al, 2008; Sinclair and Kannan, 2006; Huset et al., 2008) [**105**][**106**][**107**].

For the Fate Sees project 61 European sewage sludge samples were analysed for PFOS, PFOA, and PFNA (Table 32).

Table 33 Descriptive statistic for analyzed PFASs in sludge samples.

Number of samples: 61

	PFOA	***PFNA***	***PFOS***
U.o.m.	*ng/g*	*ng/g*	*ng/g*
Min	1,2	< DL	1,7
Max	47,5	68,1	434
Average	6,7	4,6	66,4
STD	8,3	9,5	71,2
Median	3,8	2,6	46,5
90% percentile	14,4	6,8	130
CV (%)	125	206	107
BDL (%)	0	3	0
MV (%)	0	0	3
Positive detection (%)	100	97	97

Our results are in good agreement to other data from the literature. In European sewage sludge, higher PFOS (mean: 46.5 µg/kg; max.: 434 µg/kg) than PFOA levels (mean: 3.8 µg/kg; max.: 47.5 µg/kg) are found. This is in agreement to nearly all studies from the literature. In contrast, in China sewage sludge is often higher contaminated with PFOA (Chen et al., 2012; Guo et al., 2008; Yan et al., 2012) [**108**],[**109**].

In the following graphs, average, median and 90° percentile were shown for analysed PFASs in sewage sludge samples.

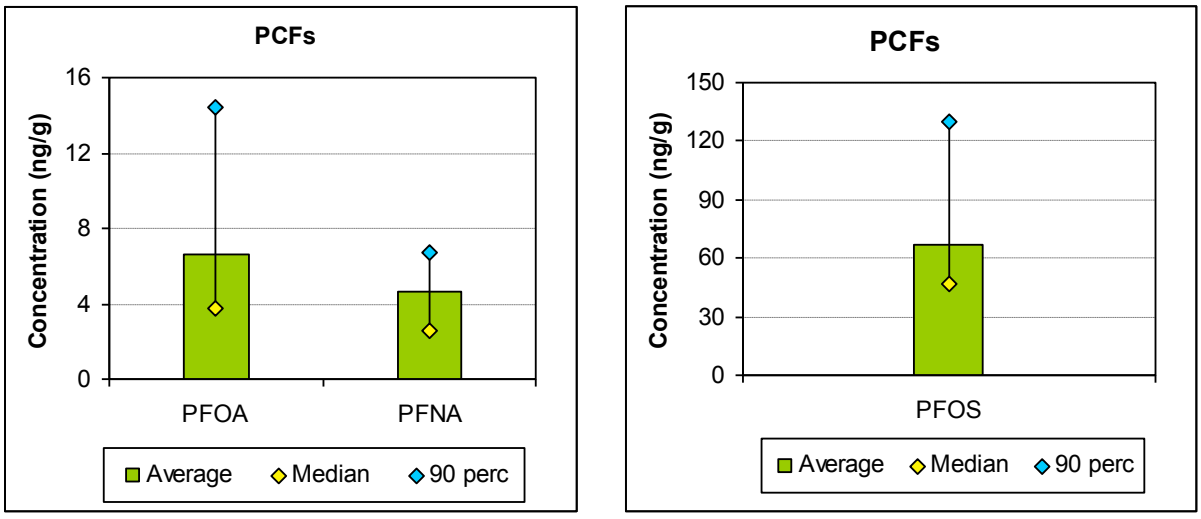


Figure 8 - Average PCM concentration, median and 90°percentile

The high coefficient of variation found for the measured PCASs was expected, because samples came from different WWTPs located in several European countries. In the following boxplots, the minimum, 1st quartile (25th percentile), 3rd quartile (75th percentile), median, and maximum are shown.

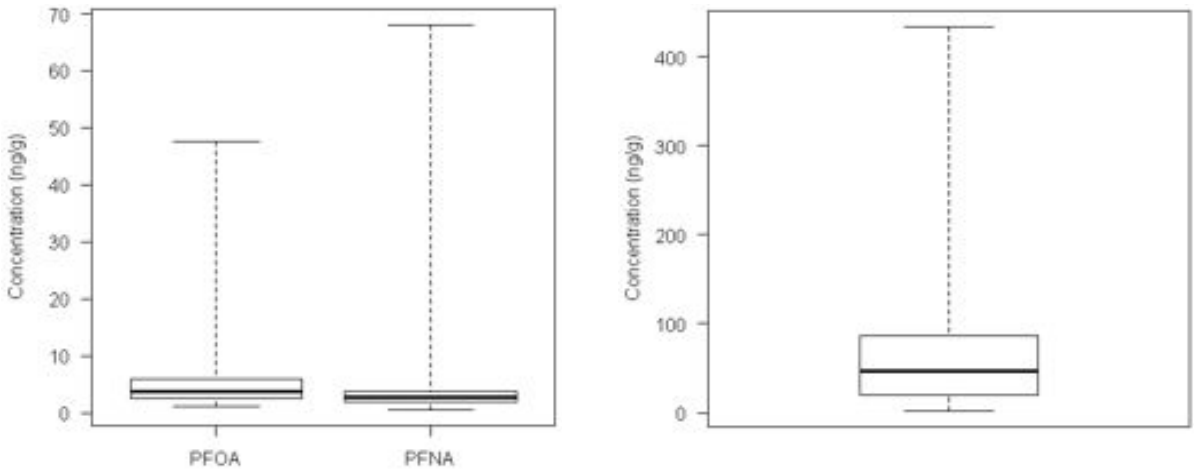


Figure 9 - Boxplots of analysed PCASs concentrations

3.3.1.5 Siloxanes

When observed values where below the LoD, LoD/2 was used as an estimate for statistical analysis. In the descriptive statistic table, the following abbreviation were used for measured compounds:

- MDM = Octamethyltrisiloxan,
- D4 = Octamethylcyclotetrasiloxan
- MD2M = Decamethyltetrasiloxan
- D5 = Decamethylcyclopentasiloxan
- MD3M = Dodecamethylpentasiloxan
- D6 = Dodecamethylcyclohexasiloxan

Table 34 - Descriptive statistic for analyzed siloxanes in sludge samples.
Number of samples: 12

	MDM	***D4***	***MD2M***	***D5***	***MD3M***	***D6***
U.o.m.	*µg/kg*	*µg/kg*	*µg/kg*	*µg/kg*	*µg/kg*	*µg/kg*
Min	<DL	<DL	<DL	2100	30	810
Max	24	2200	31	28000	250	5900
Average	-	492	-	10825	129	2824
STD	-	720	-	8492	79	1513
Median	-	107	-	6750	115	2500
90% percentile	-	1460	-	22700	220	4740
CV (%)	-	146	-	78	61	54
BDL (%)	75	33	50	0	0	0
Positive detection (%)	25	67	50	100	100	100

Given to the low number of samples analyzed, graphs and boxplots were not included.

3.3.1.6 Screening for polar emerging pollutants (negative screening)

This dataset contained not available data, which were treated like missing values. No substitution was made and statistical parameters were computed using the available number of true data only, which varies between every analyzed compound.

Table 35 - Descriptive statistic for analyzed emerging pollutants (negative screening) in sludge samples.
Number of samples: 58

	2,4-D	***2,4-Dinitrophenol***	***2,4,5-T***	***Acesulfame K***	***Acetylsalicylic acid***	***Bentazone***
U.o.m.	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*
Min	-	0,1	-	0,1	0,6	-
Max	-	4,0	-	157	563	-
Average	-	0,9	-	14,7	63,9	-
STD	-	1,0	-	28,6	102	-
Median	-	0,5	-	4,6	32,0	-
90% percentile	-	2,2	-	33,5	134	-
CV (%)	-	111	-	195	160	-
MV (%)	100	34	100	9	2	100
Positive detection (%)	0	66	0	91	98	0

	Bezafibrate	***Bromoxynil***	***Chloramphenicol***	***Clofibric acid***	***Dichlorprop***
U.o.m.	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*
Min	0,0	-	0,0	0,1	0,0
Max	6,8	-	7,6	10,5	0,5
Average	0,7	-	-	-	-
STD	1,4	-	-	-	-
Median	0,2	-	-	-	-
90% percentile	1,0	-	-	-	-
CV (%)	204	-	-	-	-
MV (%)	26	100	91	69	84
Positive detection (%)	74	0	9	31	16

	Diclofenac	***Gemfibrozil***	***Ibuprofen***	***Imidacloprid***	***Ioxynil***	***Keto-profen***
U.o.m.	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*
Min	1,3	0,3	0,2	-	-	0,3
Max	429	9,4	108	-	-	8,6
Average	43,6	-	18,2	-	-	-
STD	65,3	-	21,7	-	-	-
Median	29,2	-	10,8	-	-	-
90% percentile	70,0	-	44,8	-	-	-
CV (%)	150	-	119	-	-	-
MV (%)	19	90	28	98	100	86
Positive detection (%)	81	10	72	2	0	14

	MCPA	***Mecoprop***	***Naproxen***	***Nitrophenol***	***PFDA***	***PFHpA***	***PFNA***
U.o.m.	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*
Min	0,3	0,4	0,2	0,2	0,0	0,1	0,0
Max	2,2	1,2	9,0	22,2	69,2	23,3	10,7

	MCPA	*Mecoprop*	*Naproxen*	*Nitrophenol*	*PFDA*	*PFHpA*	*PFNA*
Average	-	-	2,6	3,7	10,7	1,9	2,3
STD	-	-	2,8	4,9	16,9	4,7	2,5
Median	-	-	1,4	2,1	5,2	0,5	0,9
90% percentile	-	-	7,4	11,2	24,2	1,7	6,7
CV (%)	-	-	105	131	158	251	112
MV (%)	95	97	41	14	43	21	31
Positive detection (%)	5	3	59	86	57	79	69

	PFOA	*PFOS*	*Saccharin*	*Sucralose*
U.o.m.	*ng/g*	*ng/g*	*ng/g*	ng/g
Min	0,2	5,3	0,6	0,0
Max	24,6	1543	72,8	19,2
Average	2,2	158	8,9	2,0
STD	3,8	274	14,0	3,4
Median	0,9	75,3	3,5	0,8
90% percentile	3,8	297	20,1	4,4
CV (%)	169	174	158	166
MV (%)	3	10	36	38
Positive detection (%)	97	90	64	62

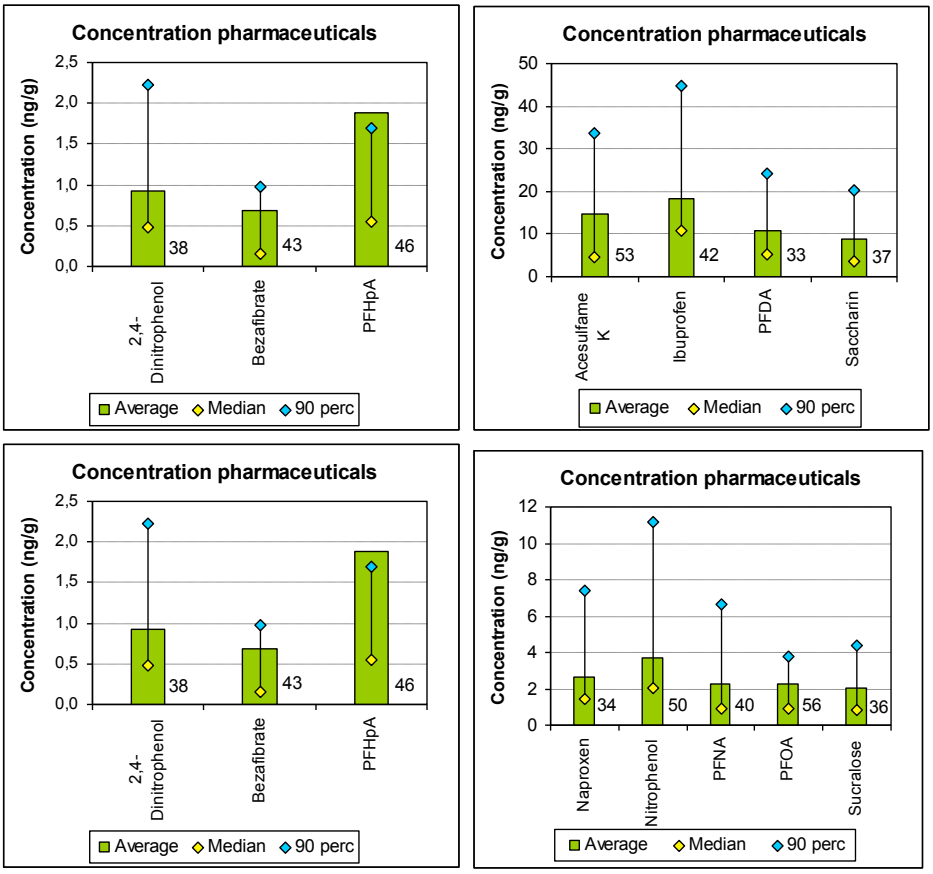


Figure 10 - Average of polar emerging pollutants (negative screening) concentration, median and 90°percentile

In graphs above, average, median and 90° percentile were shown for the analysed compounds in sewage sludge samples. Note that some perfluorinated compounds were detected only in

the screening mode, some of them in a full analytical run (see chapter 3.2.8.). From this data it appears that screening data are generally lower, but are confirmed. This indicates the validity of the screening approach to provide reasonable estimates of concentration.
The number shown on the left of the bars indicates the number of data availables to compute the statistical parameters. The high coefficient of variation found for the measured compounds was expected, because samples came from different WWTPs located in several European countries. In the following boxplots, the minimum, 1st quartile (25th percentile), 3rd quartile (75th percentile), median, and maximum are shown. The number of availables data used to create boxplots is the same indicated in the barplots.

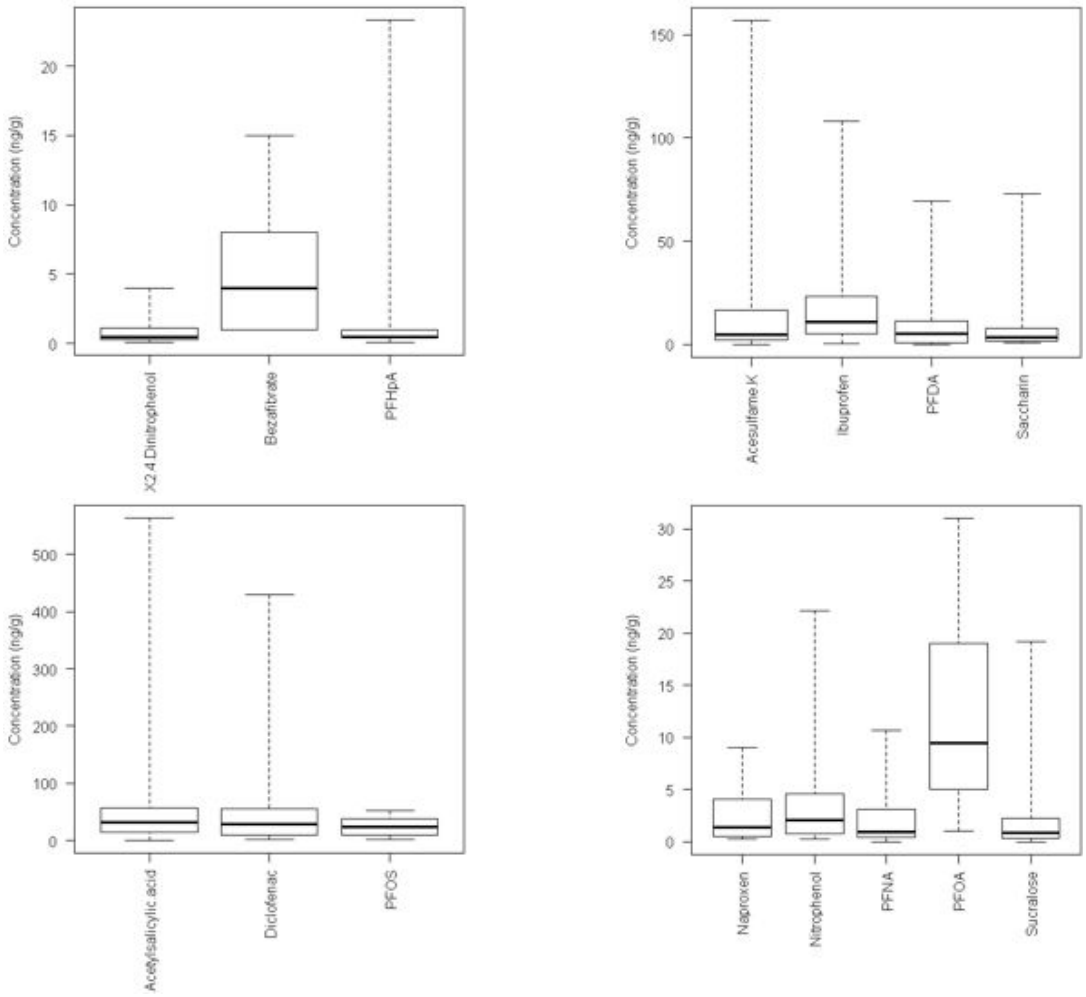


Figure 11 - Boxplots of analysed emerging pollutants (negative screening) concentrations

3.3.1.7 Screening for polar emerging pollutants (positive screening)

The dataset contained not available data, which were treated like missing values. No substitution was made and statistical parameters were computed using the available number of true data only, which varies between every analyzed compound.

Table 36 - Descriptive statistic for analyzed polar emerging pollutants in sludge samples. Number of samples: 9

	1-Methyl-1H-benzotriazole	***1H-Benzo-triazole***	***Caffeine***	***Carbendazim***	***Diuron***	***Trimethoprim***
U.o.m.	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*	*ng/g*
Min	3,57	3,97	5,62	0,54	0,15	0,01
Max	25,30	10,82	93,57	2,48	2,73	1,03
Average	12,18	7,39	25,71	1,33	1,30	0,29
STD	7,11	4,85	28,63	0,77	1,05	0,39
Median	11,40	7,39	16,84	1,07	1,58	0,14
90% percentile	21,30	10,13	47,85	2,24	2,30	0,71
CV (%)	58	66	111	58	80	136
MV (%)	11	78	11	33	44	33
Positive detection (%)	89	22	89	67	56	67

Descriptive statistics was not computed for the following substances, which were also analyzed for, because the number of positive detections was not significant:

2 positive detection: ^{1}H-Benzotriazole, Clarithromycin, Metopropol;

1 positive detection: Carbamazepine, Roxithromycin;

0 positive detection: Alachlor, Amoxicillin, Atenolol, Atrazine, Atrazine-desethyl, Atrazine-desisopropyl, Benzothiazole, Carbaryl, Carbofuran, Chloridazon, Chloridazon methyl desphenyl, Chloridazon1, Chlorotetracycline, Chlortoluron, Ciprofloxacin, DEET, Diazinon, Enrofloxacin, Erythromycin, Fenarimol, Fenitrothion, Flusilazole, Hexazinone, Iprodion, Irgarol, Isoproturon, Lincomycin, Linuron, Marbofloxacin, Methabenzthiazuron, Metolachlor, Metoxuron, Molinate, Norfloxacin, Ofloxacin, Oxytetracyclin, Propanolol, Propazine, Sarafloxacin, Simazine, Sotalol, Spiramycin, Streptomycin, Sulfadiazine, Sulfadimethoxine, Sulfamethazine, Sulfamethoxazole, Sulfathiazole, Tamoxifen, Terbutryn, Terbutylazine, Terbutylazine-desethyl, Tetracycline, Tolylfluanid.

Due to the low number of analyzed samples (9), graphs and boxplots were not produced.

3.3.2 Overview on sewage sludge regulation

In the following tables, the regulation limits for sewage sludge used in Europe are summarized. The last row of the table indicates the number of samples collected during the sewage sludge campaign, which exceed the minimum limit between different European regulations.

Table 37 - Regulation limits for sewage sludge used across Europe. Exceeding values are based on the comparison to the lowest limit value reported in the table

	As	***Cd***	***Co***	***Cr***	***Cu***	***Hg***
U.o.m.	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*
EU Limit (86/278/EEC)	-	20-40	-	na	1000-1750	16-25
Austria (Steiermark)	**20**	10	**100**	500	500	10
Belgium (Flanders)	150	6	-	250	125	5
Belgium (Walloon)	-	10	-	500	600	10
Denmark	25**	**0,8**	-	100	1000	0,8
Finland	-	1,5	-	300	600	2
France	-	-	-	-	-	-
Germany	-	10	-	900	800	8
Greece	-	20-40	-	500	1000-1750	16-25
Ireland	-	20	-	1000	1000	16
Italy	-	20	-	1000	-	10
Luxembourg	-	20-40	-	1000-1750	1000-1750	16-25
Netherlands	-	1,25	-	**75**	**75**	**0,75**
Portugal	-	20	-	1000	1000	16
*Spain***	-	20-40	-	1000-1750	1000-1750	25
Sweden	-	2	-	100	600	2,5
*Estonia**	-	15	-	1200	800	16
*Latvia**	-	20	-	2000	1000	16
*Poland**	-	10	-	500	800	5
USA	75	85	-	-	4300	57
EU proposal	-	-	-	-	-	-
Exceeding (#)	3	36	0	8	59	6

	Mo	***Ni***	***Pb***	***Sb***	***Zn***	***PAH***
U.o.m.	*mg/kg*	*mg/kg*	*mg/kg*	*mg/kg*	*%*	*ng/g*
EU Limit (86/278/EEC)		300-400	750-1200		0.25-0.40	
Austria (Steiermark)	**20**	100	500		0,2	
Belgium (Flanders)		100	300		0,09	
Belgium (Walloon)		100	500		0,2	
Denmark		30	120		0,4	**3**
Finland		100	150		0,15	
France						
Germany		200	900		0,25	
Greece		300-400	750-1200		0.25-0.4	
Ireland		300	750		0,25	
Italy		300	750		0,25	
Luxembourg		300-400	750-1200		0.25-0.4	
Netherlands		**30**	**100**			

	Mo	***Ni***	***Pb***	***Sb***	***Zn***	***PAH***
Portugal		300	750		0,25	
*Spain****		400	1200		0,4	
Sweden		50	**100**		**0,08**	**3**
*Estonia**		400	900		0,29	
*Latvia**		300	750		0,25	
*Poland**		100	500		0,25	
USA	75	420	840	**100**	0,75	
EU proposal						6
Exceeding (#)	0	10	5	0	21	

In bold the minimum regulation limit between listed values
* LOQs are matrix and run depend
** for private gardening
*** lower limit for pH < 7

3.3.3 Comparison between JRC campaign and EPA-TNSSS

As mentioned before, in the U.S. EPA-TNSSS campaign [3], sewage sludge samples were analysed for 145 pollutants, including both organic and inorganic. However, in the EPA report, average valued were available only for few chemicals. To have a comparison on concentration values for the common chemicals analysed in both the United States WWTPs (EPA) and European WWTPs (JRC), minimum and maximum values were compared. The list of common chemical is the following:

Inorganic pollutants: *Ag*, *Al*, *As*, *Ba*, *Cd*, *Co*, *Cr*, *Cu*, *Fe*, *Hg*, *K*, *Mg*, *Mn*, *Mo*, *Ni*, *P*, *Pb*, *Sb*, *Ti*, *V*, *Zn*;

PAH: *Benzo(a)pyrene*, *Fluoranthene*, *Pyrene*;

Emerging pollutants: *Caffeine*, *Carbamazepine*, *Chlorotetracycline*, *Ciprofloxacin*, *Clarithromycin*, *Enrofloxacin*, *Erythromycin*, *Gemfibrozil*, *Ibuprofen*, *Lincomycin*, *Naproxen*, *Ofloxacin*, *Oxytetracyclin*, *Roxithromycin*, *Sarafloxacin*, *Sulfadiazine*, *Sulfadimethoxine*, *Sulfamethazine*, *Sulfamethoxazole*, *Sulfathiazole*, *Tetracycline*, *Trimethoprim*;

In the following tables and graphs, minimum and maximum concentration for the common chemicals are listed. Moreover, it is to consider that different numbers of samples were compared in the two campaigns, as listed in the tables. In the EPA campaign, 84 samples were analysed for all the chemicals. In the JRC campaign, 61 samples were collected: metal were analysed in all samples, PAH in 32 samples and pharmaceuticals in 58 or 9 samples, depending on the analytical method chosen (positive or negative screening, respectively).

3.3.3.1 Metals

Table 38 - Comparison between minimum and maximum value in the EPA and JRC sewage sludge campaigns: metals concentrations

	EPA			***JRC***		
	N° detects *(positive detection/total)*	***Min***	***Max***	***N° detects*** *(positive detection/total)*	***Min***	***Max***
Ag (mg/kg)	84/84	1.94	856	58/61	< 0.06	14.66
As (mg/kg)	84/84	1.18	49.2	21/61	< 2.63	56.10
Ba (mg/kg)	84/84	75	3460	61/61	41.48	580
Cd (mg/kg)	84/84	0.21	11.8	57/61	< 0.09	5.11
Co (mg/kg)	84/84	0.87	290	61/61	1.54	16.74
Cr (mg/kg)	84/84	6.74	1160	61/61	10.79	1542
Cu (mg/kg)	84/84	115	2580	61/61	27.29	578
Hg (mg/kg)	84/84	0.17	8.3	61/61	0.10	1.13
Mn (mg/kg)	84/84	34.8	14900	61/61	75.23	960
Mo (mg/kg)	84/84	2.51	132	61/61	1.73	12.53
Ni (mg/kg)	84/84	7.44	526	61/61	8.64	310
Pb (mg/kg)	84/84	5.81	450	61/61	3.96	430
Sb (mg/kg)	72/84	0.45	26.6	40/61	< 1.66	53.6
Ti (mg/kg)	84/84	18.5	7020	61/61	65	1071
V (mg/kg)	84/84	2.04	617	61/61	2.35	135
Al (%)	84/84	0.14	5.73	61/61	0.07	5.97
Fe (%)	84/84	0.16	29.9	61/61	0.22	14.92
K (%)	84/84	-	-	54/54	0.10	2.57
Mg (%)	84/84	0.07	1.84	61/61	0.01	2.24
P (%)	84/84	0.262	11.8	54/54	1.00	5.64
Zn (%)	84/84	0.02	0.855	61/61	0.02	0.12

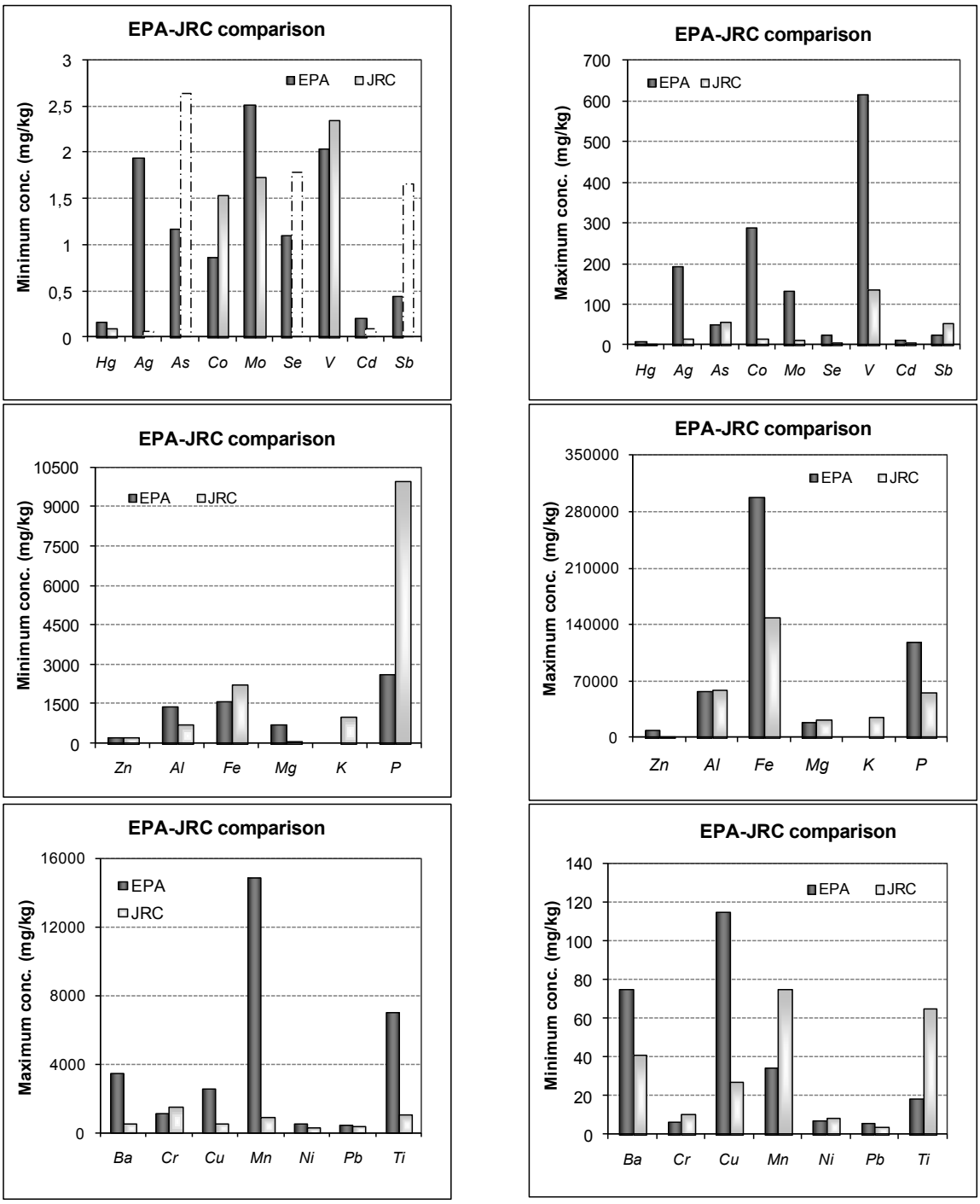


Figure 12 - Comparison between minimum and maximum metals values from EPA and JRC campaigns. Dotted white boxes for JRC data represent the detection limit value

3.3.3.2 PAH

Table 39- Comparison between minimum and maximum value in the EPA and JRC sewage sludge campaigns: PAHs concentrations

	EPA			***JRC***		
	N° detects *(positive detection/total)*	***Min (µg/kg)***	***Max (µg/kg)***	***N° detects*** *(positive detection/total)*	***Min (µg/kg)***	***Max (µg/kg)***
Benzo(a)pyrene	64/84	63	4500	32/32	18	1476
Fluoranthene	77/84	45	12000	32/32	34	3217
Pyrene	72/84	44	14000	32/32	47	2637

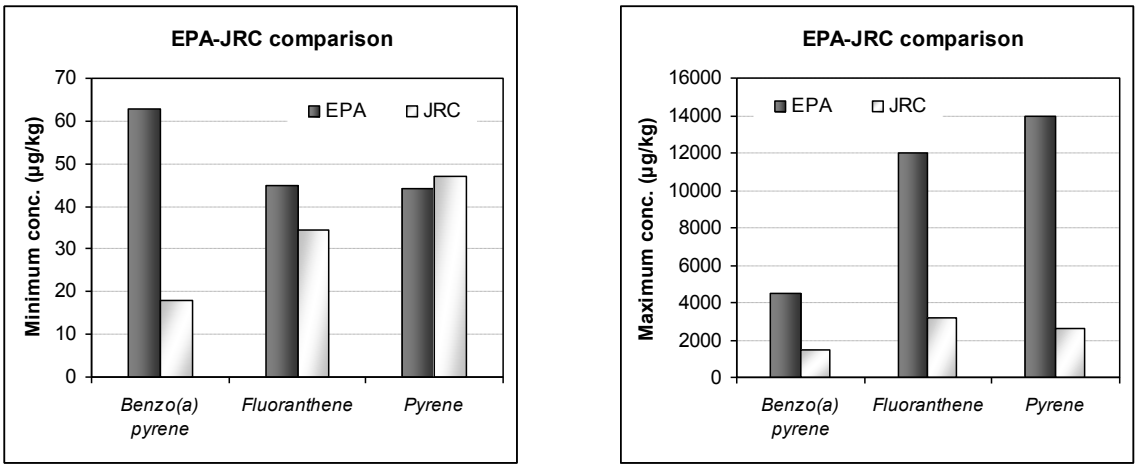


Figure 13 - Comparison between minimum and maximum PAH values from EPA and JRC campaigns

3.3.3.3 Emerging pollutants

Table 40- Comparison between minimum and maximum value in the EPA and JRC sewage sludge campaigns: pharmaceuticals concentrations

	EPA			***JRC***		
	N° detects *(positive detection/total)*	***Min (µg/kg)***	***Max (µg/kg)***	***N°detects*** *(positive detection/total)*	***Min (µg/kg)***	***Max (µg/kg)***
Gemfibrozil	76/84	12,1	2650	6/58	0,252	9,40
Ibuprofen	54/84	99,5	11900	42/58	0,162	108
Naproxen	44/84	20,9	1020	34/58	0,153	9,04
Caffeine	39/84	65,1	1110	8/9	5,62	93,6
Carbamazepine	80/84	8,74	6030	1/9	4,75	4,75
Chlorotetracycline	1/84	1010	1010	-	-	-
Ciprofloxacin	84/84	74,5	47500	-	-	-
Clarithromycin	45/84	8,68	617	2/9	0,020	3,06
Enrofloxacin	14/84	12,1	66	-	-	-

	EPA			JRC		
	N° detects *(positive detection/total)*	***Min (µg/kg)***	***Max (µg/kg)***	***N°detects*** *(positive detection/total)*	***Min (µg/kg)***	***Max (µg/kg)***
Erythromycin	77/84	3,1	180	-	-	-
Lincomycin	3/84	13,9	33,4	-	-	-
Ofloxacin	83/84	73,9	58100	-	-	-
Oxytetracyclin	29/84	18,6	467	-	-	-
Roxithromycin	3/84	14,3	22,8	1/9	1,36	1,36
Sarafloxacin	2/84	179	1980	-	-	-
Sulfadiazine	3/84	22,9	140	-	-	-
Sulfadimethoxine	5/84	3,58	62,2	-	-	-
Sulfamethazine	2/84	21,5	23,2	-	-	-
Sulfamethoxazole	30/84	3,91	651	-	-	-
Sulfathiazole	1/84	21	21	-	-	-
Tetracycline	81/84	38,3	5270	-	-	-
Trimethoprim	24/84	12,4	204	6/9	0,010	1,03

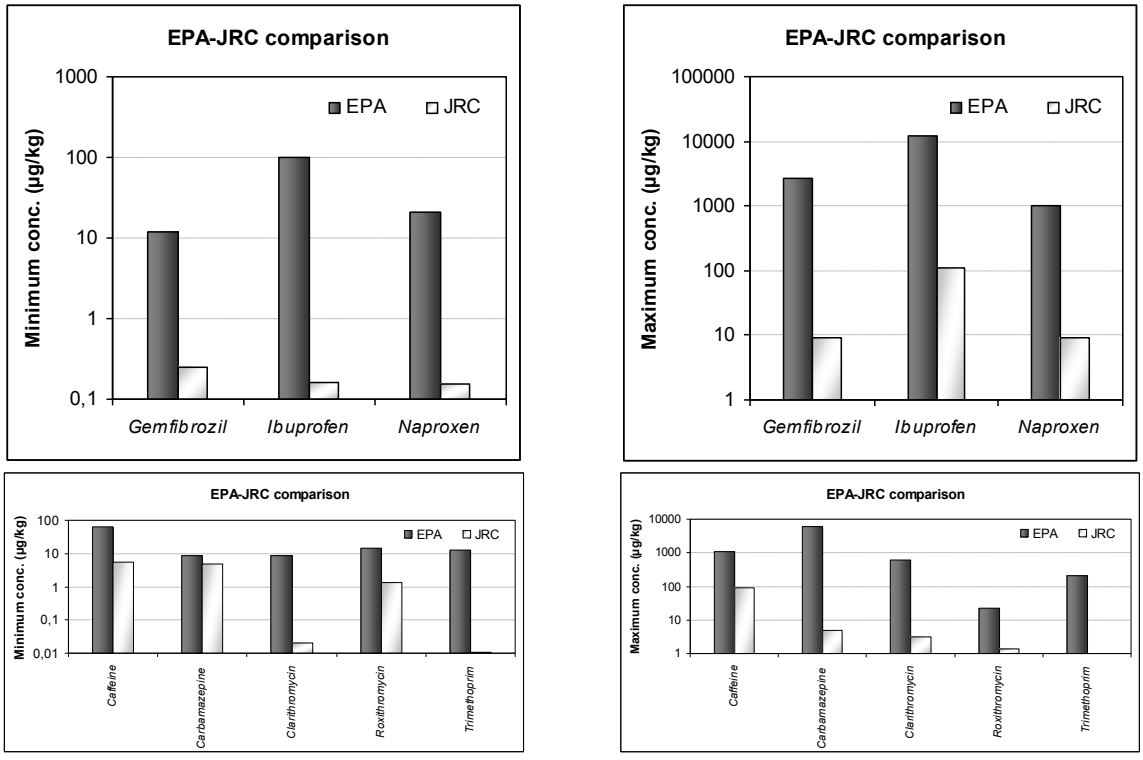


Figure 14 - Comparison between minimum and maximum pharmaceuticals values from EPA and JRC campaigns

3.3.4 Multivariate techniques

3.3.4.1 Positive matrix factorization (PMF)

Positive matrix factorization (PMF) is a recent approach to multivariate receptor modeling [**110**]. It has been widely used in air quality studies and, in recent years, it has been successfully applied to different geochemical research areas like sediments as well as soil and water compartment.

The aim of PMF application is to determine the number of factors (sources or chemical/physical processes) that had better explain the input data set variability and to find correlation among the measured variables. Markers for pollution sources as well as hidden information of the data structure may also be identified.

One of the most important characteristics of positive matrix factorization is the use of the uncertainties matrix, which allows individual weights for all the input variables to solve the factorization problem. This becomes increasingly important with the introduction of the Guide for Expression of Measurements (GUM) [**111**] and the derived Guide for Quantification of Analytical Measurements (QUAM) [**112**], which are nowadays commonly accepted references underlying numerous national and international standards.

In order to provide a qualitative identification of extracted sources, the so-called explained variations of F (EVFs) are used. They are a measure of the relative contribution of each variable in the determined sources.

Metals

PMF was applied only to the metal dataset because only for these data uncertainties were available. The data for As and Sb were omitted from the analysis because of the high percentage of below-detection-limit data (BDL). For silver and cadmium, which show <10% of BDL data, the uncensored values for BDL were used in the analysis. Potassium and phosphorus show some missing values, which were substituted by their average concentration. The error estimate matrix was built using both the LOD and the uncertainties foe each metal, computed during method validation. For BDL data the uncertainty was doubled, while for missing values the uncertainty value was multiplied by 4. Initially, the model was run varying the number o.f factors from 2 to 10.

The 4-factor central solution was chosen, because it reflected more stable data. With more than 4 factors extracted no beneficial effects were observed, being probably the additional factors caused by the isolation of single variables in unique factors; this could be due to the strong data variability within the data set. Indeed, we have to keep in mind that sludge samples were collected from WWTPs in different European countries. Factor resolution must be consisted with sources or processes common to all the selected facilities. It could thus happen that trying to force the model to explain more factors, hotspots were isolated in unique factors. Explained variations of F values characterizing the source explanation are reported in Fig. 15.

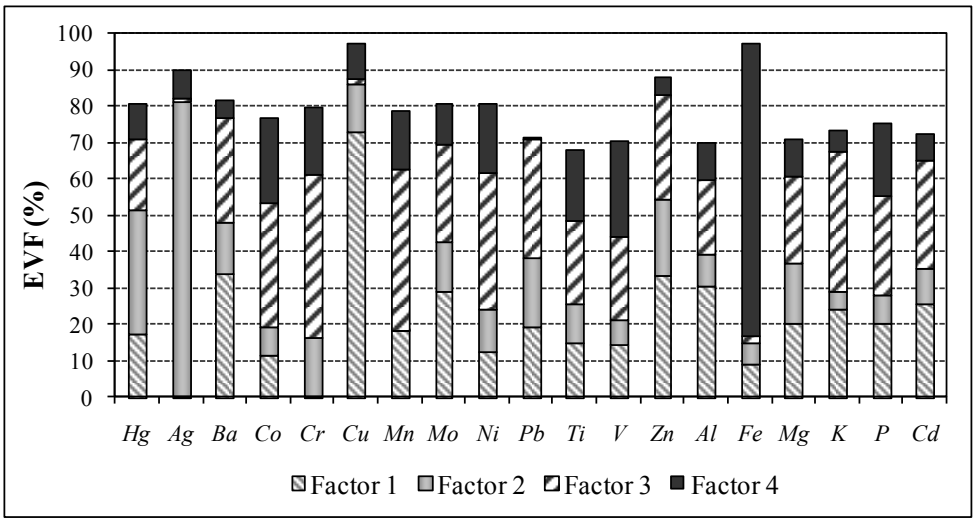


Figure 15 - Explained variation of F for the 4-factor central solution

Factor 1: Factor 1 is mainly characterized by Cu variation. Copper was found in many studies to be connected with the corrosion of domestic water pipe lines [**113**, **114**, **115**]. This element is in fact a well know plumbing material. Copper source here identified could be associated with Cu dissolution from the inner surface of a pipe by tap water.

Factor 2: This factor is mainly explained by Ag variation and, to a lower extent by Hg. The association between Ag and Hg may be due to their common behaviour with sulphur: both the elements tend in fact to react with S. However, while mercury spread its variation also in the other factors, silver shows high EVF for this source. Moreover Ag and Hg are not connected with other heavy metals, suggesting that the hypothesis of an industrial source of pollution could be rejected. Mercury was in the past used in dental amalgam, together with lower silver and other metal content. However, in factor 2 the main contribution in factor explanation is coming from silver variation. The high presence of silver could thus be associated with the environmental impact of engineering nano-Ag, which flows in municipality due to the high use of this material in household and personal care products. Although sewage systems are considered to be one of the main pathways for the release of nanosilver to the environment, no proof was produced for this was obtained here.

Factor 3: Factor 3 is characterised by the variation of the majority metals and Potassium. Due to the strong variability of sewage samples, being them collected in facilities with different characteristics, the determined source could be explained by a pollution source. This source groups all the metals, which could have an anthropogenic influence.

Factor 4: Factor 4 is defined by Fe variation. Since iron (ferrous sulphate) is one of the selected elements used for phosphorus removal at WWTPs facilities, a P-removal source was suggested. In order to have clearest source identification, G values were explored. It resulted that factor 4 assumes highest values in Finland WWTPs. Since this methodology is widely used in Finland [**116**] we can confirm the factor explanation.

3.3.4.2 Principal component analysis (PCA)

PCA, based on the singular value decomposition (SVD) algorithm, was performed using R software (R Development Core Team, 2005). Following the Kaiser criterion, principal components (PCs) with eigenvalue >1 were selected. Logarithmic transformation and autoscaling were applied to the examined data sets prior to CA application.

In contrast to PMF, PCA is a data-sensitive technique; pre-treatment of data if often necessary to obtain a data set more suitable for its application. Appropriate standardization and/or normalization procedures have to be applied prior to the analysis. In particular, normalization procedures are used to normalize data distributions, which are often apart to be normal dealing with geochemical data. The negative aspect of data pre-treatment is that different transformations can influence PCA results and data interpretation. Outliers should be removed prior to principal component analysis. Even if they can contain important information, they can negatively influence the results of the analysis

Heavy metals

PCA was initially performed only on the metals dataset to compare results obtained with PMF application

The data for As and Sb were omitted from the analysis because of the high percentage of below-detection-limit data. For silver and cadmium, which show <10% of BDL data, the uncensored values for BDL were used in the analysis. Potassium and phosphorus show some missing values, which were substituted by their average concentration. Two samples were removed from the data set because they showed strong outliers.

Logarithmic transformation and Pareto scaling were the chosen transformations applied to the dataset prior to PCA application.

Four components were extracted. Only the first three components were here reported. In the first PC, there is not a clear distinction between analyzed metals, while the second PC iron is characterized by positive loadings in Fe. PC3 was strongly dominated by Ag but differently from PMF there is no connection with Hg. Moreover, Cu is not identified with the copper release from water pipes like in PMF results.

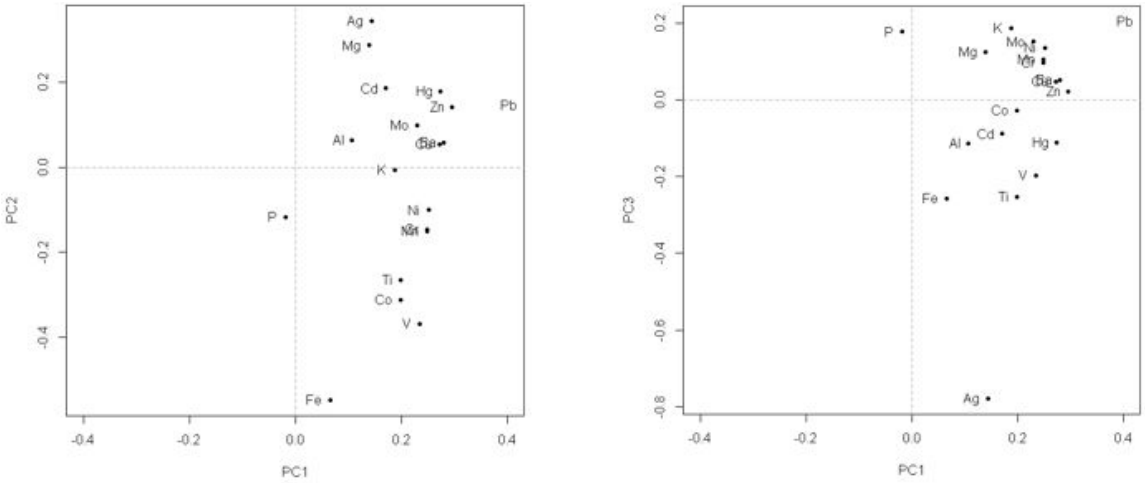


Figure 16 - Result of PCA for heavy metals

PCM and PFCs

Two samples were removed from the data set because they showed strong outliers. Logarithmic transformation and Pareto scaling were the chosen transformations applied to the dataset prior to PCA application.

The first three components were chosen. In the first two PCs, there is not a clear distinction between considered compounds, while the third PC characterized by high-negative loadings in PFOS.

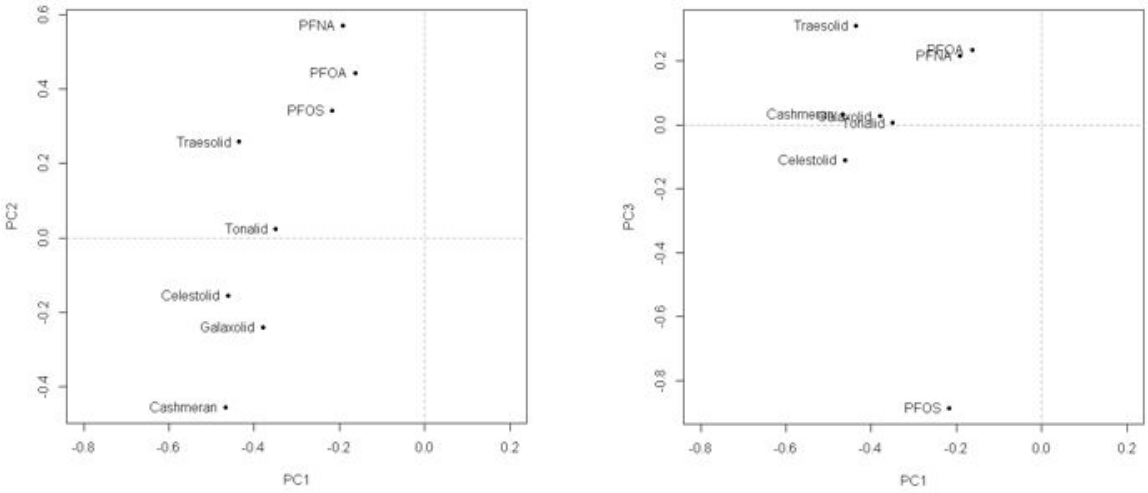


Figure 17 - PCA for PFCs and PCMs combined

Metals, PCM and PFCs

Four samples were removed from the data set because they showed strong outliers. Logarithmic transformation and Pareto scaling were the chosen transformations applied to the dataset prior to PCA application.

In the second PC, Ag show an opposite behavior respect Cashmeran and Traesolid, which are correlated, while the rest of chemicals are groped in the central part of the plot. No any other correlations results from PCA analysis in the third PC.

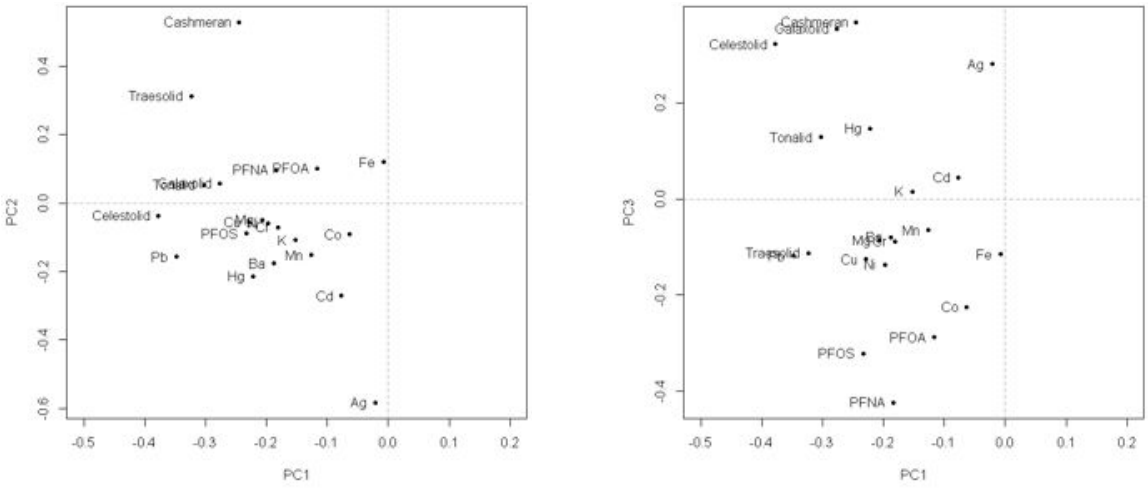


Figure 18 - PCA on combined datasets for metals, PCM and PFCs

4 Key findings and conclusions

4.1 Literature survey

- Information on the occurrence and levels of organic pollutants in sewage sludge is studied frequently and there is a growing number of publications dealing with emerging and less-investigated contaminants in this matrix. However no systematic approach to seek for these compounds is reported in a structured perspective is reported. Most papers are dealing either with known pollutants (PAHs, PCDD/Fs, PCB and alike) or are following more the intuition of the authors
- Observed concentration ranges are varying considerably, reflecting the variety of the studied environmental matrix and confirming the need of the analytical campaign performed in this study.
- In literature data, spatial coverage in case of organic pollutants is less described and documented as in case of heavy metals, which has been largely studied and reported in sewage sludge.
- Analytics for organics are challenging, often novel for emerging pollutants. Costs are higher as for the determination for heavy metals. Costs per analysis depend from different factors: the used analytical technique, imposed by the required LOD, the batch size (the wider it is, the higher discount could be applied, in the range of 10-20% of total costs) and by the ability to analyze different parameters in the same analytical run (prizes go up of about 10% per each added parameter). In more details: the analysis of 5 pesticides in water by LC-MS could costs up to 150 €; the analysis of 40 pesticides in water by LC-MS and GC-MS costs about 500 €; the cost of dioxin analysis in soil and sediment by GC-MS range from 250 to 1000 €, with an average cost of 400-450 €; PFOS analysis in LC-MS costs about 250 €. For heavy metals, mercury analysis costs 15-30 € and the analysis of the seven heavy metals indicated by the sludge directive by ICP-AES cost 70-120 €. Generally, the costs per analysis of one organic parameter result to be five-to-ten folds higher than the costs per analysis of one single heavy metal, taking into account the higher costs of the analytical
- The non-detectability of emerging compounds could often be due to the transformation of the original chemical into a more stable and persistent first degradation products coming from a first modification of functional groups, without necessarily degrading the molecular structure. Further investigation of degradation pathways would lead to a more comprehensive characterisation of sewage sludge contamination

4.2 Case study: PCDD/F and dioxin-like PCB in amended soils since 1962

- Thirty-nine years of experimental sewage sludge and compost application exceeding four times the maximal amount as laid down in Germany legislation resulted in a doubling of the international toxicity equivalent (I-TEQ) budget for PCDD/Fs and a threefold increase for DL-PCBs as compared to test plot amended with mineral fertilizer.

- As compared to mineral fertilizer, the application of farmyard manure had no effect on the PCDD/F and PCB content in soil.

- The average contribution of the DL-PCNBs to the WHO-TEQ was 19% in the mineral fertilizer and farmyard manure plots and somewhat higher in the compost (23%) and in the sewage sludge plot (27%).

- No enhancement of translocation of PCDD/Fs and PCBs into the corresponding top soils due to the presence of dissolved humic matter or other surfactants potentially present in the biowaste was observed. The similarity of congener patterns in all soils, irrespective of the type of fertilizer applied points towards atmospheric deposition of PCDD/Fs and DL-PCBs as the amin intake route in the soils. The higher levels in the sewage sludge and compost amended soils can be explained by the fact that both biowastes are subject to atmospheric deposition occurring at the origin. In the case of compost it is accumulation in the foliage, with in the case of sewage sludge, atmospheric particulate from wet and dry deposition is collected in the wastewater treatment system via urban runoff.

- It appears that the common practice of sewage sludge application iin Germany does not pose a current threat to the agro-environment with regard to PCDD/Fs and DL-PCBs.

4.3 Pan-European Screening (FATE-SEES)

- The data were collected not to characterize the efficiency of the individual WWTP/STPs, but to depict a good overview on typical situations that can be encountered for the studied compounds in European sludges.
- Measurement uncertainties (expressed as expanded uncertainties) were in the range of 3-10% for inorganic measurands and 15-25% for organic ones, with some outlying values up to 35% of uncertainty. This confirms the general performance characteristics reported by other laboratories in this domain.

4.3.1 Heavy metals

- In case of heavy metals as regulated by the Sewage Sludge Directive none of the samples exceeded the established limit. In most of the cases observed concentrations were significantly lower.
- In 11% of the analysed samples neither K nor P concentrations could be quantified with the method used. Although the method is not designed for these parameters, this result implies that future regulation on sewage sludge use in agriculture should consider the relationship between beneficial sludge properties and pollutant load.
- National limit values are in some countries significantly lower compared to the ceilings set by the Sewage Sludge Directive. Partially this recognizes the relationship between spatial and climatic influence on possible adverse effects as being discussed in the case study.

4.3.2 PAHs

- As regards PAHs for all of the studied members of this compound class median, average and 90th percentile are within the same order of magnitude, thus indicating with few exceptions are rather uniform picture. The most prominent compounds in this class were present in all samples studied.

4.3.3 PCMs

- In case of PCMs, galaxolide and tonalide were detected in all samples. Also other PCMs were present in ca. 90% of the samples. Only 50% of the samples were found positive for phantolide.

4.3.4 PFASs

- Perfluorinated surfactants were found in quantifiable amounts in all samples.

4.3.5 Siloxanes

- In case of siloxanes, three of the six studied compounds were present in all samples. Only a limited number of samples (n=12) were analysed in this case.

4.3.6 Semi-quantitative non-target screening of polar compounds

- Screening for other emerging pollutants turned out to be a useful tool to produce a first pan-European valuable dataset.
- Screening results were tended to be lower but yet comparable. A maximum of 2-5 times (so in the same order of magnitude), error that could be considered acceptable for a semi-quantitative screening method.

- None of the substances identified and semi-quantitatively measured by the screening approach was presented in all samples. The variety of ranges for the frequency of positive detection illustrates the variety of different scenarios captured by the exercise.
- The observed concentrations for the emerging pollutants were generally low (even considering the semi-quantitative nature of applied procedure for quantification and the possible underestimation of concentration data) and not alarming from a sheer concentration profile perspective.

4.3.7 Comparison between JRC campaign and EPA-TNSSS

- In case of all inorganics (exception K) and for 25 organic compounds it was possible to compare the European findings to a targeted national survey conducted by the US EPA. The comparison showed that European sludge samples featured for the regulated inorganics generally slightly lower values if compared to the US. In case of emerging pollutants, US data appeared to be significantly higher than concentration observed in European sludges.

4.3.8 Statistical analysis

- Multivariate analyses did not reveal significant correlations nor non-correlations between inorganics and, PCMs and PFCs. Only partial overlap was observed. Hence it cannot be concluded that due to different behavior and occurrence patterns, organics would require additional European legislation for organics.

4.3.9 Main conclusion

- Both the snapshot exercise and the experience of the US EPA Targeted National Survey on Sewage Sludge, revealed the usefulness to occasional survey the occurrence organic pollutants. It might be worth to consider a repetition of the exercise maybe including more countries, rather than regulate single compounds.
- The monitored concentrations do not justify the introduction of new limit values for the considered parameters.
- The dataset available and the case study considered revealed no scientific evidences to introduce a regulation for classical POPs.
- Concerning the huge variety of emerging pollutants, there are no evidences to require a regulation, with the exception of PFASs, moreover included in the Stockholm Convention, which exhibit a different environmental pathway than classical apolar POPs.

Most of Member States have internal regulations stricter than the present Sewage Sludge Directive. (The introduction of new stricter regulation, for example in Germany, has been imposed to remedy cases of bad management of sewage sludge use and not by the real need to decrease the set limit values).

5 References

1 86/278/EEC Council Directive of 12 June 1986 on the protection of the environment, and in particular of the soil, when sewage sludge is used in agriculture

2 MILIEU ENVIRONMENTAL LAW & POLICY, WRC & RPA. Environmental, economic and social impacts from the revision of the Sewage Sludge Directive, http://ec.europa.eu/environment/waste/sludge/pdf/part_iii_report.pdf (last visited 18th of July 2012)

3 EPA (2009). Targeted National Sludge Survey. Sampling and Analysis Technical Report. http://water.epa.gov/scitech/wastetech/biosolids/upload/2009_01_15_biosolids_tnsss-tech.pdf (last visited 18th of July 2012)

4 Communication from the Commission to the Council and the European Parliament on future steps in bio-waste management in the European Union {SEC(2010) 577}, COM/2010/0235 final, http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=COM:2010:0235:FIN:EN:PDF (last visited 18th of July 2012)

5 European Commission (2000), Working Document on Sludge. Third Draft, Brussels 27 April 2000, DG Environment http://ec.europa.eu/environment/waste/sludge/pdf/sludge_en.pdf (last visited 18th of July 2012)

6 Katsoyiannis A., Samara C., 2005, Persistent organic pollutants (POPs) in the conventional activated sludge treatment process: fate and mass balance, Environ Res. (97), 245-257

7 Muezzinoglu A., 2003, A study of volatile organic sulfur emissions causing urban odors, Chemosphere (51), 245-252

8 S. Rasi S., Veijanen A., Rintala J., 2007, Trace compounds of biogas from different biogas production plants, Energy (32), 1375-1380

9 Nicholls C.R., Allchin C.R., Law R.J., 2001, Levels of short and medium chain length polychlorinated n-alkanes in environmental samples from selected industrial areas in England and Wales, Environ Poll. (114), 415-430

10 Katsoyiannis A., Samara C., 2004, Persistent organic pollutants (POPs) in the sewage treatment plant of Thessaloniki, northern Greece: occurrence and removal, Wat. Res (38), 2685-2698

11 Oberg K., Warman K., Oberg T., 2002, Distribution and levels of brominated flame retardants in sewage sludge, Chemosphere (48), 805-809

12 Eljarrat E., Marsh G., Labandeira A., Barcelo D., 2008, Effect of sewage sludges contaminated with polybrominated diphenylethers on agricultural soils, Chemosphere (71), 1079-1086

13 Kupper T., de Alencastro L.F., Gatsigazi R. Furrer R., Grandjean D., Tarradellas J., 2008, Concentrations and specific loads of brominated flame retardants in sewage sludge, Chemosphere (2008), 1173-1180

14 Brandli R. C., Kupper T., Bucheli T. D., Zennegg M., Huber S., Ortelli D., Muller, D., Schaffner Ch., Iozza S., Schmid P., Berger U., Edder P., Oehme M., X. Stadelmann F.X., Tarradellas J., 2007, J Environ. Monit. (9), 465-472

15 Voulvoulis N., Lester J. N., 2006, Fate of organotins in sewage sludge during anaerobic digestion, Sci. Tot. Environ (371), 373-382

16 Becker A.M., Gerstmann S., Frank H., 2008, Perfluorooctane surfactants in waste waters, the major source of river pollution, Chemosphere (72), 115-121

17 de Voot P., et al., 2006, Perforce project, Perfluorinated organic compounds in the European Environment, 15 September 2006. http://www.science.uva.nl/perforce/index.htm?http%3A//www.science.uva.nl/perforce/publicat.htm (last accessed on 20th of July 2012)

18 Gomez M.J., Martinez Bueno M.J., Lacorte S., Fernandez-Alba A.R., Aguera A., 2007, Pilot survey monitoring pharmaceuticals and related compounds in a sewage treatment plant located on the Mediterranean coast, Chemosphere (66), 993-1002

19 Beausse J., 2004, Selected drugs in solid matrices: a review of environmental determination, occurrence and properties of principal substances, Trends Anal Chem (23), 753-761

20 Carballa M., Omil F., Lema J.M., Llompart M., Garcia-Jares C., Rodriguez I., Gomez M., Ternes T., 2004, Behavior of pharmaceuticals, cosmetics andhormones in a sewage treatment plant, Wat Res. (38), 2918-2926

21 Vieno N. M., Tuhkanen T., Kronberg L., 2006, Analysis of neutral and basic pharmaceuticals in sewage treatment plants and in recipient rivers using solid phase extraction and liquid chromatography–tandem mass spectrometry detection, J Chromatogr A. 1134(1-2):101-111

22 Golet E.M., Xifra I., Siegrist H., Alder A., Giger W., 2003, Environmental Exposure Assessment of Fluoroquinolone Intibacterial Agents from Sewage to Soil, Environ Sci Technol (37), 3243-3249

23 Lindberg R., Wennberg P., Johansson M.I., Tysklind M., Andersson B. V., 2005, Screening of Human Antibiotic Substances and Determination of Weekly Mass Flows in Five Sewage Treatment Plants in Sweden, Environ. Sci. Technol. (39), 3421-3429

24 Stasinakis A. S., Gatidou G., Mamais D., Thomaidi N. S., Lekkas T. D., 2008, Occurrence and fate of endocrine disrupters in Greek sewage treatment plants, Wat. Res. (42), 1796-1804

25 Herren D., Berset J.D., 2000, Nitro musks, nitro musk amino metabolites and polycyclic musks in sewage sludges. Quantitative determination by HRGC-ion-trap-MS/MS and mass spectral characterization of the amino metabolites, Chemosphere (40), 565-574

26 Kupper T., Berset J.D., Etter-Holzer R., Furrer R., Tarradellas J., 2004, Concentrations and specific loads of polycyclic musks in sewage sludge originating from a monitoring network in Switzerland, Chemosphere (54), 1111-1120

27 Llompart M., Garcia-Jares C., Salgado C., Polo M., Cela R., 2003, D etermination of musk compounds in sewage treatment plant sludge samples by solid-phase microextraction, J Chromatography A (999), 185-193

28 Andreu V., Ferrer E., Rubio J. L., Font G., Picó Y., 2007, Quantitative determination of octylphenol, nonylphenol, alkylphenol ethoxylates and alcohol ethoxylates by pressurized liquid extraction and liquid chromatography-mass spectrometry in soils treated with sewage sludges. Sci Total Environ. 378(1-2): 124-129

29 Bester K., 2004, Retention characteristics and balance assessment for two polycyclic musk fragrances (HHCB and AHTN) in a typical German sewage treatment plant, Chemosphere (57), 863-870

30 Sanchez-Brunete C., Miguel E., Tadeo J. L., 2008, Determination of organochlorine pesticides in sewage sludge by matrix solid-phase dispersion and gas chromatography–mass spectrometry, Talanta (74), 1211-1217

31 Diaz-Cruz M. S, Barcelo D., 2006, Highly selective sample preparation and gas chromatographic–mass spectrometric analysis of chlorpyrifos, diazinon and their major metabolites in sludge and sludge-fertilized agricultural soils, J. Chromatography A 1132(1-2): 21-27

32 Kupper T., Plagellat C., Brandli R.C., de Alencastro L.F., Grandjean D., Tarradellas J., 2006, Fate and removal of polycyclic musks, UV filters and biocides during wastewater treatment, Wat. Res. (40), 2603-2612

33 Krogh P.H., Verge Lopez C., Cassani G, Jensen J., Holmstrup M., Schraepen N., Jørgensen E., Gavor Z., Temara A., 2007, Risk assessment of linear alkylbenzene sulphonates, LAS, in agricultural soil revisited: Robust chronic toxicity tests for Folsom

34 Petersen S.O., Henriksen K., Mortensen G.K., Krogh P.H., Brandt K.K., Sørensen J., Madsen T. , Petersen J., Grøn C., 2003, Recycling of sewage sludge and household compost to arable land: fate and effects of organic contaminants, and impact on soil fertility, Soil & Tillage Research 72 (2003) 139–152

35 Abad E., Martinez K., Planas C., Palacios O., Caixach J., Rivera J., 2005, Priority organic pollutant assessment of sludges for agricultural purposes, Chemosphere (61), 1358-1369

36 Vikelsøe J., Thomsen M., Carlsen L., 2002, Phthalates and onylphenols in profiles of differently dressed soils, Sci. Tot. Environ. (296), 105-116

37 Fountoulakis M., Drillia P., Pakou C., Kampioti A., Stamatelatou K, Lyberatos G., 2005, Analysis of nonylphenol and nonylphenol ethoxylates in sewage sludge by high performance liquid chromatography following microwave-assisted extraction, Journal of Chromatography A, 1089 (2005) 45–51

38 Bolz U., Hagenmaier H., Korner W., 2001, Phenolic Xenoestrogens in surface water, sediments and sewage sludge from Baden-Wurttemberg , south- west Germany, Environ Poll. (115), 291-301

39 Schowanek D., Carr R., David H, Douben P., Hall J., Kirchmann H., Patria L., Sequi P., Smith S., Webb S., 2004, A risk-based methodology for deriving quality standards for organic contaminants in sewage sludge for use in agriculture—Conceptual Framework, Regulatory Toxicology and Pharmacology 40 (2004) 227–251.

40 Aparicio I., Santos J.L., Alonso E., 2007, Simultaneous sonication-assisted extraction, and determination by gas chromatography–mass spectrometry, of di-(2-ethylhexyl)phthalate, nonylphenol, nonylphenol ethoxylates and polychlorinated biphenyls in sludge from wastewater treatment plants, Analytica Chimica Acta 584 (2007) 455–461

41 Marttinen S. K., Kettunen R. H., Rintala J. A., 2003, Occurrence and removal of organic pollutants in sewages and landfill leachates, Sci. Tot Environ (301), 1-12

42 Galvez A., Conesa J. A., Martin-Gullon I., Font R., 2007, Interaction between pollutants produced in sewage sludge combustion and cement raw material, Chemosphere (69), 387-394

43 Stevens J.L., Green N.J.L., Bowater R.J., Jones K.C., 2001, Interlaboratory comparison exercise for the analysis of PCDD/F in samples of digested sewage sludge, Chemosphere (45), 1139-1150

44 Stevens J.L., Nicholas J.L., Green J.L., Jones K.C., 2001a, Survey of PCDD/Fs and non-ortho PCB in UK sewage sludge, Chemosphere (44), 1455-1462

45 Martínez K, Abad E, Palacios O, Caixach J, Rivera J., 2007 Assessment of polychlorinated dibenzo-p-dioxins and dibenzofurans in sludges according to the European environmental policy. Environ Int. 33(8), 1040-1047

46 Mantis I., Voutsa D., Samara C., 2005, Assessment of the environmental hazard from municipal and industrial wastewater treatment sludge by employing chemical and biological methods, Ecotoxicol Environ Safety (62), 397-407

47 Blanchard M., Teil M.J., Ollivon D., Legenti L., Chevreuil M., 2004, Polycyclic aromatic hydrocarbons and polychlorobiphenyls in wastewaters and sewage sludges from the Paris area (France), Environ Res. (95), 184-197

48 Benabdallah El-Hadj T., Dosta J., Torres R., Mata-Álvarez J., 2007, PCB and AOX removal in mesophilic and thermophilic sewage sludge digestion, Biochem. Eng. J. (36), 281-287

49 Jarde E., Mansuy L., Faure P., 2005, Organic markers in the lipidic fraction of sewage sludges, Wat Res (39), 1215-1232

50 Perez S., Guillamon, M., Barcelo D., 2001, Quantitative analysis of polycyclic aromatic hydrocarbons in sewage sludge from wastewater treatment plants J Chromatography A (938), 57-65

51 Perez S., la Ferre M., Garcia M.J., Barcelo D., 2001, Occurrence polycyclic aromatic hydrocarbons in sewage sludge and their contribution to its toxicity in the ToxAlert® 100 bioassay, Chemosphere (45), 705-712

52 Oleszczuk P., 2008, Phytotoxicity of municipal sewage sludge composts related to physico-chemical properties, PAHs and heavy metals, Ecotox Environ Safety (69), 496-505

53 Santos J.L., Aparicio I., Alonso E., 2007, A new method for the routine analysis of LAS and PAH in sewage sludge by simultaneous sonication-assisted extraction prior to liquid chromatographic determination, Anal Chim Acta (605), 102-109

54 Busetti F., Heitz A., Cuomo M., Badoer S., Traverso P., 2006, Determination of sixteen polycyclic aromatic hydrocarbons in aqueous and solid samples from an Italian wastewater treatment plant, J Chromatography A (1102), 104-115

55 Chaler R., Simoneit B.R.T., Grimalt J.O., 2001, Bile acids and sterols in urban sewage treatment plants, J Chromatography A (927), 155-160

56 Petrovic M., Barcelo D., 2000, Determination of Anionic and Nonionic Surfactants, Their Degradation Products, and Endocrine-Disrupting Compounds in Sewage Sludge by Liquid hromatography/Mass Spectrometry, Anal Chem (72), 4560-4567

57 Scott M. J., Jones M. N., 2000, The biodegradation of surfactants in the environment, Biochimica and Biophysica Acta (1508), 235-251

58 Carlsen L., Metzon M-B, Kjelsmark J., 2002, Linear alkylbenzene sulfonates (LAS) in the terrestrial environment Sci Tot Environ (290), 225-230

59 Gonzalez S., Petrovic M., Barcelo D., 2004, Simultaneous extraction and fate of linear alkylbenzene sulfonates, coconut diethanol amides, nonylphenol ethoxylates and their degradation products in wastewater treatment plants, receiving coastal waters and sediments in the Catalonian area (NE Spain), J Chromatogr A. 1052(1-2), 111-120.

60 Rodriguez I., Calvo F., Quintana J.B., Rubi E., Rodil R., Cela R., 2006, Suitability of solid-phase microextraction for the determination of organophosphate flame retardants and plasticizers in water samples, J Chromathography A (1108), 158-165

61 Chapmann H., Purnell K., law R. J., Kirby M. F., The use of chemical dispersants to compabt oil spills at sea: A review of practice and research needs in Europe, Marine Poll Bull., (54), 827-838

62 Hoekstra E. (1999). On the natural formation of chlorinated organic compounds in soil. PhD Thesis, Vrije Universiteot Amsterdam, pp 273.

63 Gawlik B.M., Sotiriou N., Feicht E.A., Schulte-Hostede S., Kettrup A., 1997, Alternatives for determination of the soil adsorption coefficient, Koc, of non-inorganic compounds- a review, Chemosphere 34, 2525-2551

64 Gawlik B.M., Kettrup A., Muntau H., 2000, Estimation of soil adsorption coefficients of organic compounds by HPLC screening using the second generation of the European reference soil set, Chemosphere (41), 1337-1347

65 Lang V., 1992, Polychlorinated biphenyls in the environment, J. Chromatogr A (595), 1-43

66 Jabusch T.W., Swackhamer D.L., 2005, Partitioning of polychlorinated biphenyls in octanol/water triolein/water, and membrane/water system, Chemosphere (60), 1270-1278

67 Huckins, J. N., Petty, J. D., Lebo, J. A., Almeida, F. V., Booij, K., Alvarez, D. A., Cranor, L. W., Clark, R. C.,Mogensen, B. B. 2002. Development of the Permeability/Performance Reference Compound Approach for In Situ Calibration of Semipermeable Membrane Devices. Environ. Sci. Technol. 36: 85-91.

68 Falandysz J, Brudnowska B, Kawano M, Wakimoto T, 2001. Polychlorinated biphenyls and organochlorine pesticides in soils from the southern part of Poland. Arch Environ Contam Toxicol, 40: 173–178.

69 Khan SJ, Ongerth JE. Estimation of pharmaceutical residues in primary and secondary sewage sludge based on quantities of use and fugacity modeling. Water Sci Technol 2002;46:105–13.

70 Jones, O.A.H., Voulvoulis, N., Lester, J.N., 2002. Aquatic environmental assessment of the top 25 English prescription pharmaceuticals. Water Res. 36, 5013–5022.

71 Umlauf G., Christoph e., Lanzini L., Savolainen R., Skejo H., Bidoglio G., Clemens J., Goldbach H., Schere H., PCDD/D and dioxin-like PCB porfiles in soils amended with sewage sludge, compost, farmyard manure and mineral fertilizer since 1962, Environ Sci Pollut res (2011), 18:462-470

73 Vymazal J., 2007, Removal of nutrients in various types of constructed wetlands, Sci. Tot. Environ. (380), 48-65

74 Eickhout B., Bouwman A.F., van Zeijts H., 2006, The role of nitrogen in world food production and environmental sustainability, Agriculture, Ecosystems and Environment 116:4-14

75 Falkengren-Grerup U., ten Brink D-J., Brunet J., 2006, Land use effects on soil N, P, C and pH persist over 40-80 years of forest growth on agricultural soils, Forest Ecol. Manage. (225), 74-81

79 Council Directive 91/271/EEC of 21 May 1991 concerning urban waste-water treatment, http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31991L0271:EN:HTML (last accessed 24th of July 2012)

80 Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources, http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31991L0676:EN:HTML (last accessed 24th of July 2012)

81 Pastor L., Marti N., Bouzas A., Seco A., 2008, Sewage sludge management for phosphorus recovery as struvite in EBPR wastewater treatment plants, Bioresource Technol. (99), 4817-4824

82 Donner D., Salecker M., 1999, Elimination of phosphorus from waste water by crystallization, Environ. Technol. (20), 735-742

83 Pentera R.G., Reali M.A.P., Foresti E., Campos J.R., 1999, Post-treatment of effluents from anaerobic reactor treating domestic sewage by dissolved-air flotation, Water Sci. Technol. (40), 137-143

84 Baker M.J., Blowes D.W., Ptacek C.J., 1998, Laboratory development of permeable reactive mixtures for removal of phosphorus from onsite wastewater disposal system, Environ. Sci. Technol. (32), 2308-2316

85 Ojeda G., Tarrasón D., Ortiz O., Alcaniz J.M., 2006, Nitrogen losses in runoff waters from a loamy soil treated with sewage sludge, Agricul. Ecocyst. Environ. (117), 19-56

86 Bowes M.J., House W.A., Hodgkinson R.A., 2003, Phosphorus dynamics along a river continuum, Sci. Tot. Environ. (313), 199-212

87 Hernández T., Moral R., Perez-Espinoza A., Moreno-Caselles J., Perez-Murcia M.D., Garcia C., 2002, Nitrogen mineralisation potential in calcareous soil amended with sewage sludge, Biosource Technol. (83), 213-219

88 Bowes M.J., Hilton J., Irons G.P., Hornby D.D., The relative contribution of sewage and diffuse phosphorus sources in the River Avon catchment, southern England: Implications for nutrients management, Sci. Tot. Environ. (344), 67-81

89 Krogerus K., Ekholm P., 2003, Phosphorus in settling matter and bottom sediments in lakes loaded by agriculture, Hydrobiologia (429), 15-28

90 Neal C., Jarvie H.P., Neal M., Hill L., Wickham H., 2006, Nitrate concentrations in river waters of the upper Themes and its tributaries, Sci. Tot. Environ. (365), 15-32

91 Neal C., Jarvie H.P., Neal M., Hill L., Wickham H., 2006, Nitrate concentrations in river waters of the upper Themes and its tributaries, Sci. Tot. Environ. (365), 15-32

92 Jarvie H.P., Neal C., Withers P.J.A., Robinson A., Salter N., Nutrient water quality of the Wye catchment, UK: exploring patterns and fluxes using the Environment Agency data achieves, Hydrol. Eart Syst. Sci. (7) 5, 722-743

93 B. M. Gawlik, R. Loos, G. Bidoglio, G. Fauler, X. Guo, E. Lankmayr, Th. Linsinger, 2012, Testing sample stability in shortterm isochronous stability studies for EU-wide monitoring surveys of polar organic contaminants in water, Trends in Analytical Chemistry 36, 36-46

94 European Standard prEN 16174 (2010). Sludge, treated biowaste and soil – digestion of aqua regia soluble fractions of elements.

95 European Standard prEN 16170 (2010). Sludge, treated biowaste and soil – Determination of trace elements by inductively coupled plasma optical emission spectrometry (ICP-OES).

96 Powley, C.R., George, S.W., Ryan, T.W., Buck, R.C. **2005**. Matrix effect-free analytical methods for determination of perfluorinated carboxylic acids in environmental matrixes. Analytical Chemistry 77, 6353-6358.

97 Jahnke, A., Berger, B. **2009**. Trace analysis of per- and polyfluorinated alkyl substances in various matrices - How do current methods perform? Journal of Chromatography A 1216, 410–421.

98 Van Leeuwen, S.P.J., et al. **2011**. IVM, Amsterdam. Third interlaboratory study on perfluorinated compounds in environmental and human matrices, Report R-11/04; 27 May 2011

99 Lindstrom, A.B., Strynar, M.J., Laurence Libelo, E. **2011a**. Polyfluorinated compounds: past, present, and future. Environ. Sci. Technol. 45, 7954-7961.

100 OECD, **2002**. ENV/JM/RD(2002)17/Final, Hazard Assessment of Perfluorooctane Sulfonate (PFOS) and its Salts.

101 Zhou, Q., Deng, S., Zhang, Q., Fan, Q., Huang, J., Yu, G. **2010**. Sorption of perfluorooctane sulfonate and perfluorooctanoate on activated sludge. Chemosphere 81, 453-458.

102 Sepulvado, J.G., Blaine, A.C., Hundal, L.S., Higgins, C.P. **2011**. Occurrence and fate of perfluorochemicals in soil following the land application of municipal biosolids. Environ. Sci. Technol. 45, 8106–8112.

103 Washington, J.W., Yoo, H., Jackson Ellington, J., Jenkins, T.M., Laurence Libello, E. **2010**. Concentrations, distribution, and persistence of perfluoroalkylates in sludge-applied soils near Decatur, Alabama, USA. Environ. Sci. Technol. 44, 8390-8396.

104 Hölzer, J., Göen, T., Just, P., Reupert, R., Rauchfuss, K., Kraft, M., Müller, J., Wilhelm, M. **2011**. Perfluorinated compounds in fish and blood of anglers at Lake Möhne, Sauerland Area, Germany. Environ. Sci. Technol. 45, 8046-8052.

105 Becker A.M., Gerstmann S., Frank H. **2008**. Perfluorooctane surfactants in waste waters, the major source of river pollution. Chemosphere 72, 115-121.

106 Sinclair, E., Kannan, K. **2006**. Mass loading and fate of perfluoroalkyl surfactants in wastewater treatment plants. Environ. Sci. Technol. 40, 1408-1414.

107 Van Leeuwen, S.P.J., et al. **2011**. IVM, Amsterdam. Third interlaboratory study on perfluorinated compounds in environmental and human matrices, Report R-11/04; 27 May 2011

108 Chen, H., Zhang, C., Han, J., Yu, Y., Zhang, P. **2012**. PFOS and PFOA in influents, effluents, and biosolids of Chinese wastewater treatment plants and effluent-receiving marine environments. Environmental Pollution 170, 26-31.

109 Yan, H., Zhang, C.-J., Zhou, Q., Chen, L., Meng, X.-Z. **2012**. Short- and long-chain perfluorinated acids in sewage sludge from Shanghai, China. Chemosphere 88, 1300-1305.

110 PhD Comero

111 BIPM 2008, Evaluation of measurement data — Guide to the expression of uncertainty in measurement, http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf (last accessed on 24th of July 2012)

112 EURACHEM 1995. Quantifying uncertainty in analytical measurements, Ellison SLR, Roesslein M, Williams A (eds), 1st edition, EURACHEM.

113 Fjällborg B, Dave G (2003) Toxicity of copper in sewage sludge Environ Int. 28(8):761-769

114 Fabbricino M, Panico A, Trifuoggi M (2005), Copper release in drinking water due to internal corrosion of distribution pipes, Global NEST Journal 7 (2), 163-171

115 Houhou, J.; Lartiges, B. S.; Hofmann, A.; Frappier, G.; Ghanbaja, J.; Temgoua, A., (2009). Phosphate dynamics in an urban sewer: A case study of Nancy, France. Water Res., 43 (4), 1088-1100

116 I. Ruotsalainen, 2011, Wastewater treatment planst in the Baltic sea drainage basin - A Master of Science thesis. http://civil.aalto.fi/en/research/water/theses/ruotsalainen2011.pdf (last accessed 25th of July 2012)

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Abstract

This report describes the technical support provided to identify and prioritize among relevant compounds that have to be considered in European regulation dealing with Sewage Sludge. The work includes the results of a screening of typical European situations of sewage sludges with regard to the occurrence and levels of compounds of concern, many of which never assessed in a pan-European dimension. In total, 63 samples originating from 15 countries, were assessed for 22 minor and trace elements and 92 organic compounds including ingredients of personal care products and pharmaceuticals. Obtained results are assessed statistically and where possible compared to other findings. Background information from literature describing the situation before the survey is included. To assess the availability of selected persistent organic pollutants, findings of along-term case study are included, too.

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